NOVEMBER, 1952

Journal of METALS

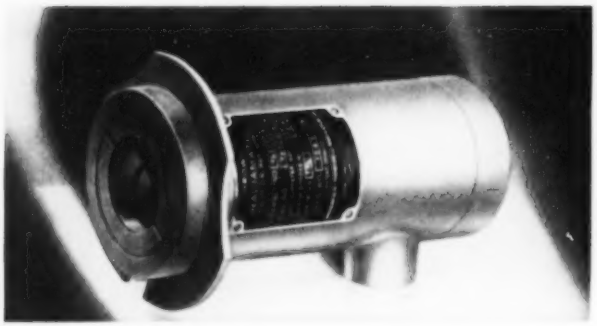
November JOURNAL OF METALS Highlights:

"Germanium Has Become of Primary Importance" - p. 1132

"Small Additions Raise Hot Strength of Zirconium" - p. 1138

"Electrolytic Zinc Plant at Monsanto, Ill." - p. 1149

Radiamatic Pyrometers . . .



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Journal of **METALS**

VOL. 4, NO. 11 NOVEMBER, 1952

COVER

A heat of Ductile Iron is poured at the Bayonne Research Laboratory foundry of International Nickel Co. The brilliant flash at the beginning of the pour is caused by magnesium, which is used to produce the spheroidal graphite structure that characterizes Ductile Iron. See story p. 1143.

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Greater Size and Speed in Aircraft have created engineering problems, the solution of which has required larger and larger forgings of high-strength aluminum alloy. Examples shown above are forged structural members used in a modern military bomber, the largest more than seven feet over all. These are forged on an 18,000-ton press, the biggest ever built in this country.

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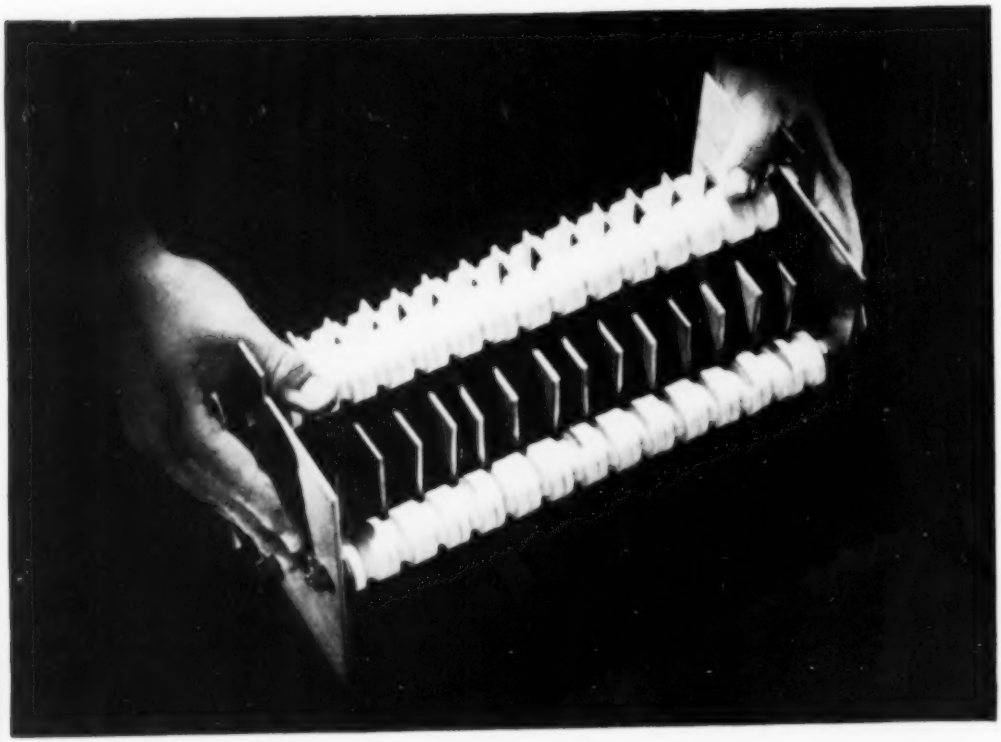

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This guinea pig test is typical of the many and varied research projects sponsored by United States Steel to help you get the most out of the steel you use. We invite you to make use of our facilities to help solve any problem you may have involving the more efficient use of steel. Simply write to United States Steel, Room 2806H, 525 William Penn Place, Pittsburgh 30, Pa.

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MEET THE AUTHORS

W. Chubb (p. 1138), a member of the Ohio Valley Section, AIME, enjoys mineralogy, gardening, and photography as his hobbies. Born in Washington, D. C., Mr. Chubb is a graduate of the Missouri School of Mines and Metallurgy (B.S., M.S.). From 1949 to 1951 he was an assistant engineer for the Brush Beryllium Co., and then joined Battelle Memorial Institute where he is principal metallurgist.

J. R. Musgrave (p. 1132) is chief physicist with the research laboratories of Eagle-Picher Co., Joplin. He was born in Reading, Pa. and attended Lafayette College and the University of Toronto. Dr. Musgrave was engaged in biological chemistry and had also been on the staff at the University of Toronto before joining Eagle-Picher in 1935.

W. CHUBB

J. R. MUSGRAVE

Colman Goldberg (p. 1160) is a graduate of Wayne University (B.S. 1948); Northwestern University (M.S. 1949 and Ph.D. 1951). After receiving his doctorate, Dr. Goldberg joined the Westinghouse Research Laboratories as a research physicist. Now residing in Penn Township, he is a member of the American Physical Society.

J. H. Richards (p. 1162) is a graduate of Carnegie Institute of Technology (1942, B.S.). Mr. Richards was born in McKeesport, Pa. and is presently residing in Pittsburgh. From 1942 to 1944 he was a contract employee for the U. S. Naval Research Laboratory at Anacosta, D. C. He was also in the Navy and then joined the U. S. Steel Co. as research associate in steelmaking and rolling practices. He is a member of AIME and ASM. Photography and golf occupy him in his free time.

A. D. SCHWOPE

T. I. MOORE

A. D. Schwope (p. 1138) was born in Milwaukee, and attended Marquette University and Ohio State University. For three years Mr. Schwope was metallurgist at Wright Aeronautical Co. In 1946 he joined Battelle Memorial Institute where he is now supervisor of mechanical metallurgy. In his spare time Mr. Schwope enjoys tennis and entomology. A member of the Ohio Valley Section of AIME, he has presented papers covering creep and recrystallization of copper.

T. I. Moore (p. 1149) assistant general superintendent, American Zinc Co. of Ill., was born in Iola, Kan. A graduate of Ohio State University he joined the American Zinc Oxide Co., Columbus, Ohio as plant engineer in 1930. He then was transferred to Fairmont City, Ill. as plant engineer. In 1939 he was at Dumas, Texas in the position of chief engineer. From 1941 to 1944 Mr. Moore was made assistant general superintendent. For two years he was a lieutenant in the Navy and upon his discharge returned to American Zinc Co. of Ill., Monsanto. A member of the AIME St. Louis Section, he is interested in politics, residential construction, and naval reserve training.

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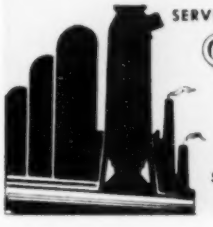

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Plating Foreman with minimum of five years' plating experience. Some supervisory experience preferred. Salary up to $4500 a year. Location, Connecticut. Y7562(g).

Metallurgical Chemist, chemical or metallurgical graduate, with 2 to 3 years' experience for corrosion research on nonferrous alloys. Salary, $4000 a year. Location, northern New Jersey. Y7569.

Powder Metallurgist with a few years' practical experience for the development of powder metal products of many varieties of metals and shapes and the design of the plant and equipment to make them in quantity. Salary open. Location, western Pennsylvania. Y7561.

Mechanical Draftsman on tools, for sheet metal work. Must be U. S. citizen. Salary, $3900 to $4420 a year. Location, Long Island City, N. Y. Y7530.

Metallurgists, 3, recent graduates, with at least three years' experience covering ferrous and nonferrous materials for test work, preparation of material specifications, heat treatment, welding, annealing at heavy industry manufacturing plant. Location, central Pennsylvania. Y6111.

Metallurgist, preferably with 2 to 3 years experience or an M.S. degree, for work in connection with nonferrous vacuum processing. Location, New York. Y7370(a).

Graduate Metallurgist for job analysis. Salary, $4160 a year to start. Location, New Jersey. Y7374(b).

Metallurgist, preferably with 2 to 3 years' experience or an M.S. degree, for work in connection with nonferrous vacuum processing. Location, New York. Y7370(a).

Sales Engineer, 25 to 40, with two years of college engineering, preferably married, with metallurgical, chemical, mechanical, or electrical degree, and three to five years' experience selling industrial equipment for application and sale of industrial burner systems by mail and by direct personal solicitation. Field travel away from home frequently required. Salary, $4800 to $6000 a year. Company will pay fee. Location, New York. Y7337.

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Metallurgist, 33, desires position in development, technical operations, or as technical writer. Major experience includes 3 years in electrolytic refining, 3 years metallurgical chemist. Lesser experience in powder metals development, physical testing, observer, steel mill. M-709.

Metallurgical - Mechanical Engineer, experienced in laboratory, foundry, weld fabrication and machine shop, ferrous and nonferrous metals, desires production or development work in East. Married, age 33. M-701.

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SCHOOL OF MINES

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Applications are invited for the Krumb Scholarships and Campbell Fellowships for the academic year 1953-54. These are available to candidates for degrees in the fields of Mining, Metallurgy and Metallurgical Engineering.

The Krumb Scholarships, with stipends of $1000 and $500 respectively, in New York City, are in support of studies toward the B.S., M.S. or professional engineering degrees. Preference is given to students in mining engineering in the rank of three in the field of metallurgical and metallurgical engineering.

The Campbell Fellowships, established to encourage research in the general field of metals, are available to candidates for graduate and professional degrees pursuing the Ph.D. Five graduate fellowships, $1000 each, with stipends of $1000 for single students and $2000 for married students. Application blanks and further information may be obtained on request to the Office of University Admissions, Columbia University, New York 27, N. Y. Completed applications should be submitted before Feb. 20, 1953.

METALLOGRAPHER

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Box H-19, JOURNAL OF METALS

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METALLURGIST, research, age 40. Recovery of nonferrous metals from ores (southern area), applying furnace, electrolytic, and leaching methods. Experience with copper, silver, zinc, cadmium, selenium, tin, lead, and others. Also metal powders.

Box P-12, JOURNAL OF METALS

METALLURGIST. A recent graduate is desired for research and development work in copper, titanium and other metals. This is an opportunity for a permanent position with a progressive and highly successful company in southern New England. Please give details of education, experience and salary.

Box H-20, JOURNAL OF METALS

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Mechanical or Metallurgical Engineering graduate with foundry experience. Desire man with mechanical aptitude, research ability, and experience. To work in development section of laboratories of nationally known Midwest nonferrous industry. State qualifications and salary expected in first letter.

Box J-21, JOURNAL OF METALS

METALLURGIST. Recent graduate in metallurgical or mechanical engineering for development work in nationally known Midwest nonferrous industry. One to two years' experience desirable but not essential. State qualifications and salary expected in first letter.

Box J-22, JOURNAL OF METALS

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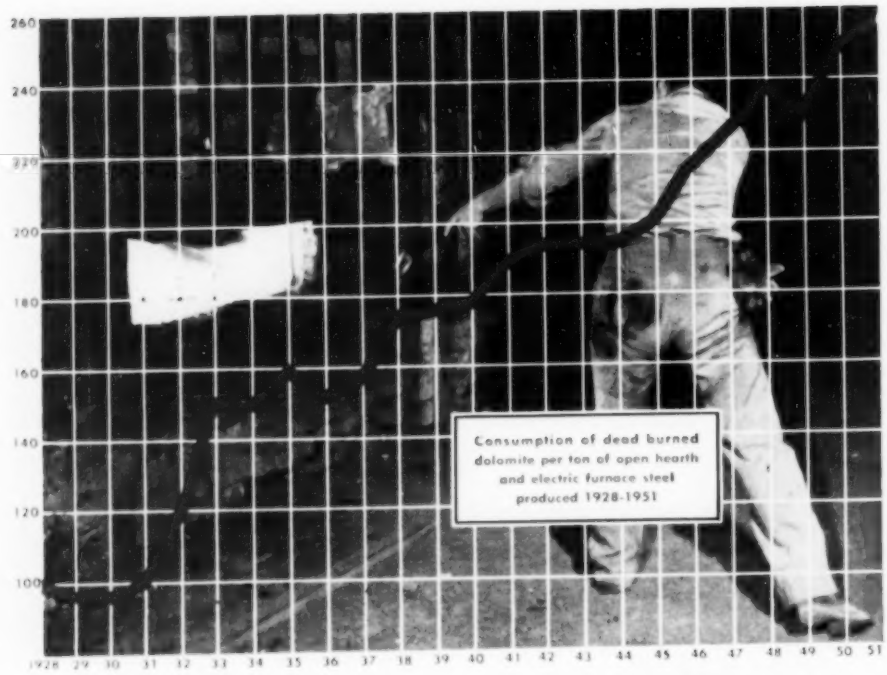

raw dolomite vs. dead burned dolomite

RAW dolomite is without peer for routine "drying" of open hearth bottoms and is useful for banking doors and making up banks over the line. However, for bank and bottom maintenance, most operators have concluded that despite its low price raw dolomite is not a low cost refractory.

The difference in price between dead burned dolomite and raw dolomite is essentially a reflection of the difference in the amount of work performed on the two products by the supplier. The increase in refractory value exceeds the increase in price because of characteristics imparted to dead burned dolomite during processing.

To obtain the oxides of calcium and magnesium, the desired refractory constituents, dolomite must be calcined to drive off carbon dioxide amounting to about 50% of its weight. In the case of dead burned dolomite fuel for calcination is provided by the manufacturer, whereas with raw dolomite it is supplied by the steelmaker. The average lime kiln uses about 10,000,000 BTU's to produce a ton of calcined product. Thus in making a 200-ton heat, an open hearth using 100 pounds of raw dolomite per ton of steel, consumes enough fuel in calcination to refine 15 tons of steel!

Merely to get the same number of pounds of refractory oxides contained in a ton of dead burned dolomite requires handling about 2 tons of raw dolomite, with a like reduction in furnace capacity. However, substitution of raw dolomite on a 2 to 1 basis fails to recognize the vastly superior efficiency of dead burned dolomite as a maintenance refractory. The coalescing agent incorporated in dead burned dolomite during manufacture causes the refractory to *set fast and stay fast* at operating temperatures. Concurrently each grain is "shrunk" to about 17% of its original volume and sized to insure a well consolidated repair of maximum density and refractory oxide content.

In contrast raw dolomite calcines to high porosity and low density in the open hearth and in the absence of an integral bond sets erratically under the fluxing effect of slag soaked up from bank and bottom.

These are some of the factors that have dictated the steady 25-year swing to dead burned dolomite. During this period Basic Refractories' capacity for producing its dead burned dolomite products, Magnefer and Syndolag, has been expanded repeatedly to meet steelmakers' needs.

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1—TESTING MACHINE: Deluxe model super L hydraulic universal testing machine has been announced by *Tinius Olsen Testing Machine Co.* These machines handle much larger specimens with high accuracy. They are built in capacities of 60,000, 120,000, 200,000, 300,000, 400,000, 500,000, and 600,000 lb.

2—CASTING REPAIR: A kit has been introduced by the *American Metaseal Corp.* to repair casting defects on the spot. All materials needed to repair defects in ferrous or nonferrous castings including pin holes, blow holes, cracks, chips, and machining cuts are contained in the kit.

3—POURING UNIT: The Ajaxomatic, a new automatic unit for pouring accurate amounts of molten metal into molds, has been announced by the *Ajax Engineering Corp.* It is designed to discharge molten metal, in particular aluminum, directly into the cold chamber of most available die casting machines. Molten metal is taken from

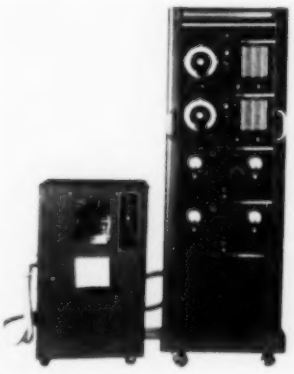
a point considerably below the surface of the melt, eliminating any chance for pouring surface oxides or scum into the casting. It can also be used for zinc alloys and the normal range is for castings from ½ to 5 lb. Castings up to 20 lb can be produced with slight modifications.

4—ROLL NECK GAGING: Accuracy to within 0.0001 in. in gaging of roll necks is possible with this new gage developed by the *Timken Co.* This new air gage measuring system also has possibilities for use in checking crowns on both work rolls and back-up rolls in rolling mills.

5—PORTABLE NIBBLER: Heavy duty portable nibbler cuts 14 gage stainless steel, galvanized iron, and softer materials in proportion without distortion on either side. The minimum cutting radius of this machine is ⅞ in. *Fenway Machine Sales Co.*

6—THROWOVER PANEL: A new automatic throwover panel, a control device that transfers electric circuits to an emergency power source when the normal source fails, has been announced by the *General Electric Co.*

7—SCALER-PRINTER: Instrument designed for radiation counting as applied in nuclear work, packaging, and other applications has been introduced by *North American Philips Co., Inc.* It indicates in printed numerals up to 999 and provides for



multiplying this figure by 2, 4, 8, 16, 32, and 64. The instrument counts electronically, stores the counts in a memory circuit, and after completion of the counting interval, channels the memorized count into a mechanical printer.

8—INDUCTION HEATING: A new 50 kw unit has been added to the *Lindberg Engineering Co.* line of high frequency induction heating units. Specifications are: Output, 50 kw, 2840 btu per min, 400,000 cycles per sec, input, 230, 460, 550 v, 3 phase, 60 cycle, 100 kva max, 90 pct power factor, 3 kva idling. Average water consumption at full load is 22.5 gpm, pressure 20 to 80 lb.

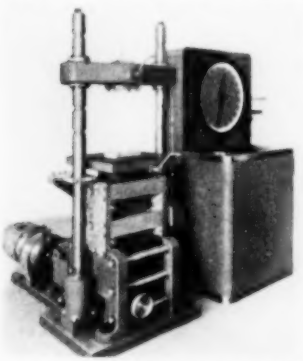
9—SPLICER: Development of guillotine splicer unit and splicer clips has been announced by the *Masco Mfg. Co.* Advantages claimed are elimination of heating, manual bending, and tied ends; heat number of coil can be stamped on clip, providing positive quality control. This equipment offers a fast, more efficient way to connect the wire ends of coils for drawing through patenting furnaces.

10—VIBRATRON: Electronic machine for analysis, evaluation, and correction of vibration has been developed by the *International Research & Development Corp.* It will measure amplitude and frequency of vibration and discover the source, and operates on 110v 60c current.

11—DRILLING MACHINE: A semiautomatic drilling, boring, and facing machine for producing aircraft jet engine compressor housings has been developed by *Modern Industrial Engineering Co.* It has four motor operated heads located at 45° positions around the index table.

12—METAL-CUTTING SAW: A metal-cutting saw features segments which are locked together by flexible tightening pins instead of rivets. Saws are available in diameters from 11 to 63 in. with various tooth spacings for cutting ferrous or nonferrous metals. *Henry Disston & Sons, Inc.*

13—TESTING MACHINE: A new type of universal testing machine incorporating an electric weighing



system and electronically controlled, motor driven loading mechanism has been announced by *Baldwin-Lima-Hamilton Corp.* The model has a capacity of 50,000 lb load. Three load ranges are provided on a separate indicator with 24-in. diam dial having 1000 gradations in 66 in.: 0-50,000 lb, 0-10,000 lb, and 0-2000 lb.

14—THERMOCOUPLE WIRES: Three new thermocouple wires suitable for use in temperatures varying from −20 to 2000 F are available from *Minneapolis-Honeywell Regulator Co.*

Free Literature

20—TOOL STEEL: Bulletin issued by *Joseph T. Ryerson & Son, Inc.*, gives technical data on Ry-Die, a 5 per chromium type air hardening tool and die steel. It is suitable for drawing, blanking and forming dies, gages, forming rolls, and punches.

21—HEAT TREATING: *Pressed Steel Co.* has issued a general catalog featuring the firm's line of heat treating equipment. Installation views of new equipment, various types of tubing for annealing, firing cabinet furnaces, and fixtures used in carburizing are included.

22—HEAT EXCHANGER TUBES: Welded aluminum heat exchanger tubes are made by longitudinally butt welding Alclad 3S-H12 aluminum alloy sheet rather than drawing seamless aluminum tubes. Advantages, fabrication, and applications are listed in brochure available from *Aluminum Co. of America*.

23—LIQUID FLAME HEATING: Report 24 obtainable from *Ajax Electric Co., Inc.* describes this commercially proven application. Advantages are fast and uniform heating, no oxidation, scaling or decarburization, flexibility, and low costs.

24—CUT OFF MACHINE: Folder describes the complete line of specimen cut-off machines. Five models are available for samples from ½ to 3 in. diam. *Buehler Ltd.*

25—BARREL PLATING: Descriptions of models C and Super E are included in bulletin issued by *Frederic B. Stevens, Inc.* Several special applications for this automatic barrel machine are described in detail and pictures are included.

26—HYDRAULIC CYLINDERS: Diagrams, photographs, and charts explain the different mounting types and capacities of *Leadberg Engineering Co.* hydraulic cylinders up to 1500 and 3000 psi working pressure.

27—SCREW COVER HEAD: Bulletin 3601 covers a new multi-purpose screw type thermocouple head. It can be used for single or duplex thermocouple or resistance thermometer terminal blocks and is protected against freeze-up and rust. *Minneapolis-Honeywell Regulator Co.*

28—LIQUID POLYMER: A viscous liquid which converts to a tough, resilient, solvent-resistant rubber at room temperature is described in folder released by the *Thiokol Corp.*

29—CU ALLOY SPECIFICATIONS: A revised edition of copper and copper alloy specification index has been issued by the *American Brass Co.* Specifications of various engineering societies and government agencies, including military are listed.

30—OPTICAL STRAIGHTEDGE: System for measuring surface flatness by means of optical levels that utilize a beam of light as a straight line reference is explained in catalog 20. *Gramcold Mfg. Co.*

31—WATER SOFTENERS: Troubles caused by utilization of hard water and multiple economies effected by curing them are discussed in bulletin 2306 available from the *Permutit Co.* The three basic types of ion exchange equipment are explained and how to properly utilize them is shown.

32—TUNNEL BURNER ASSEMBLIES: Catalog 897 released by *Hauck Mfg. Co.* will be of interest to industrial plants doing heat processing. Twenty sizes of tunnel burner assemblies are listed for natural or artificial gas.

33—FLUOBORATE SOLUTIONS: New booklet outlines how Baker and Adamson metal fluoborate solutions are used in many applications. Data are also included on the chemical and physical properties of the various concentrates. *Allied Chemical & Dye Corp.*

34—SIGNAL TEMPERATURE CONTROL: *Thermo Electric Co., Inc.* recently published catalog section 55 illustrating and describing thermo electronic signaling temperature controller and resistance bulbs.

35—METALLOGRAPHY EQUIPMENT: Test specimens are common metals and alloys mounted, and supplied with photomicrograph, analysis, hardness, etc., for comparison or teaching. *A. I. Buehler.*

36—TEMPILAQ®: Instruction sheet for using Tempilaq® has been issued by the *Tempil Corp.* Special techniques are discussed.

37—GRINDING BANDS: Line grind bands which are used on band machines to machine very hard materials such as hardened steels and abrasive and brittle materials are discussed in bulletin 49-810 available from *DoAll Co.* Complete information as to type of grits available in these bands and applicability of these grits to different machining jobs is also discussed.

38—GEAR MATERIALS: Part I and Part II issued by the *International Nickel Co., Inc.* gives information on modern trends in gear materials, nickel, steel and cast iron; and new gear materials.

39—X-RAY SPECTROMETRY: Folder containing drawings, charts and photographs, presents all important details concerning operating principles and uses of this technique. *North American Philips Co., Inc.*

40—PNEUMATIC CONTROLLER: The new P-4 Pneumatrol pneumatic controller, for rate of flow, differential pressure, liquid level, viscosity, pressure, and temperature applications, a product of *Fischer & Porter Co.*, is described in catalog C-50. The unit is a true motion balance controller and not the force balance system commonly employed in point-of-measurement (stack) controllers.

41—PRODUCT DEVELOPMENT: A service bridging the gap between the research and development engineering phase on one hand and the regular production for commercial purposes on the other is described in brochure issued by the *Cambridge Corp.*

Journal of Metals
29 West 39th St
New York 18, N. Y.

November

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ELECTROMET *Data Sheet*

A Digest of the Production, Properties, and Uses of Steels and Other Metals

Published by Electro Metallurgical Company, a Division of Union Carbide and Carbon Corporation, 30 East 42nd Street, New York 17, N. Y. • In Canada: Electro Metallurgical Company of Canada, Limited, Welland, Ontario

How VANADIUM improves engineering steels and helps conserve critical alloys

In these critical times when many alloying materials are scarce, you may be able to use vanadium to good advantage. Steels alloyed with vanadium meet most of the mechanical specifications for low-alloy engineering and structural steels. In fact, vanadium can often be used in engineering steels to replace at least part, if not all, of certain alloys now in critical supply.

The metallurgy of vanadium is well known. Small additions of vanadium—0.10 to 0.25 per cent—can be used effectively to give steel extra strength, toughness, and resistance to fatigue and wear. It improves engineering steels by increasing their yield strength without sacrificing ductility. The uniformly fine grain size of vanadium-bearing steels makes them tough and resistant to abrasion, fatigue, and impact.

Better Mechanical Properties

In the following table are typical analyses for carbon-vanadium and chromium-vanadium steels that are suitable for most applications where low-alloy, high-strength steels are required. The carbon-vanadium steel is compared with plain carbon steel, and the chromium-vanadium steel, with chromium-molybdenum steel. Note the excellent properties of the vanadium-bearing steels.

Fig. 1 — Vanadium increases the strength, toughness, and wear resistance of engineering steels for many machine parts, such as this large crankshaft.

Improves Cast Iron

A small addition of vanadium, usually from 0.10 to 0.25 per cent, refines the grain of cast iron, and materially increases its strength and hardness. Moreover, vanadium may be used in cast iron to replace at least part, if not all, of certain alloys that are now in short supply.

Vanadium in Rimmed Steel

An addition of approximately 1 lb of vanadium per ton of steel produces non-aging characteristics in a rimmed steel. These non-aging properties, together with improved deep-drawing characteristics and the good surface inherent in rimmed steels, make these steels of particular interest at the present time.

Grades of Ferrovanadium

ELECTROMET produces ferrovanadium containing 50 to 55 per cent vanadium for the production of vanadium-bearing steels and irons. The alloy is produced in three grades with maximum 0.20, 0.50, or 3.00 per cent carbon and maximum 1.50, 2.00, and 8.00 per cent silicon, respectively. Each grade is specially adapted to fill the different requirements of iron- and steel-making.

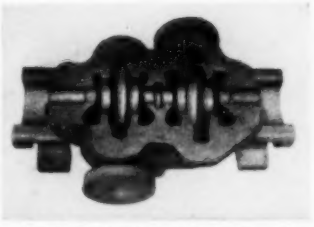

Fig. 2—Steel and iron castings treated with small additions of vanadium have high ductility and greater toughness and impact resistance.

Write for a copy of the booklet, "ELECTROMET Products and Service," which gives helpful information about the use of ferrovanadium and other alloying metals that ELECTROMET supplies. The booklet may be obtained from any ELECTROMET office: in Birmingham, Chicago, Cleveland, Detroit, Los Angeles, New York, Pittsburgh, or San Francisco. In Canada: Welland, Ontario.

Properties of Vanadium Steels Compared With Other Engineering Steels

Typical Analysis, %	Carbon Steel	Carbon-Vanadium Steel	Chromium-Molybdenum Steel	Chromium-Vanadium Steel
Vanadium	—	0.16	—	0.16
Carbon	0.50	0.49	0.50	0.50
Manganese	0.71	0.77	0.80	0.79
Silicon	0.19	0.15	0.30	0.31
Chromium	—	—	0.95	0.98
Molybdenum	—	—	0.20	—
Annealed and Furnace-Cooled				
Tensile Strength, psi	90,600	100,000	100,000	99,500
Yield Point, psi	48,900	66,000	50,000	64,100
Elongation in 2 in., %	23.3	25.0	23.0	28.4
Reduction of Area, %	37.8	49.1	45.0	59.0
Izod Impact, ft.-lb.	13.5	26.0	17.0	44.0
Quenched and Tempered				
Tensile Strength, psi	134,900	134,500	232,000	232,800
Yield Point, psi	110,800	128,000	214,500	224,200
Elongation in 2 in., %	18.3	18.3	10.0	10.4
Reduction of Area, %	54.1	56.6	39.0	43.1
Izod Impact, ft.-lb.	54.0	65.0	12.0	12.0

The term "Electromet" is a registered trademark of Union Carbide and Carbon Corporation.

Books for Engineers

Handbook of Nonferrous Metallurgy. Donald M. Liddell, editor-in-chief. McGraw-Hill Book Co., $8.00, second edition, Vol. I, 856 pp., 1945.—In this edition, an attempt has been made to treat only the reduction and refining of metals and to the main to omit considerations of their working and utilization after production. Work with copper, lead and similar metals, the largest matter of the chapter, is the extraction of the metal from the ore, in the case of magnesium and aluminum where it is unlikely that the engineer will be called upon to design a reduction works much of the space is devoted to the useful alloys of the metal. There is much that is elementary. The book is designed for student as well as the engineer and the cost-

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Metallurgical Equilibrium Diagrams. by W. Hume-Rothery, J. W. Christian, and W. B. Pearson. *The Institute of Physics*, $7.00, 311 pp., 1952.—The book begins with a theoretical introduction, followed by details of general laboratory technique, and the different methods of pyrometry. A full description of experimental methods for the determination of the liquidus, including special chapters on high melting alloys follows. Sections deal with the determination of the solidus, solid solubility curves, and the use of X-ray methods. The last section covers ternary systems from both the theoretical and experimental viewpoint. Illustrations are included.

Lead in Modern Industries. *Lead Industries Assn.*, $1.50, 230 pp., 1952.—The book has been prepared for the purpose of gathering into one volume a large amount of general and technical information for use of metallurgists, chemists, engineers, and executives. Through the use of the assembled information, it is hoped that they will be able to determine whether lead can aid them in their specific projects. No claim for completeness is made. The book begins with a brief history of lead, and continues with an account of the metals travel from mine to finished product. It treats forms and fabricating processes, storage batteries, cables, corrosion resistance, welding, and other topics.

Calculus of Variations. by Robert Weinstock. *McGraw-Hill Book Co.*, $6.50, 326 pp., 1952.—Following a brief treatment of classical elementary problems, the author plunges into the role of calculus of variations in particle dynamics, geometrical optics, quantum mechanics, elasticity, electrostatics, and in the eigenvalue problems associated with the vibrating string and vibrating membrane. Techniques and underlying ideas are stressed.

Chemical Engineering Operations. by Frank Rumford. *Chemical Publishing Co. Inc.*, $7.50, 376 pp., 1952.—The book's purpose is to introduce processes peculiar to chemical plant operation. The author's approach is to survey a plant which has been developed using the method under discussion. He then gives an analysis of the underlying principles without attempting exhaustive treatment. Where necessary, examples are given to illustrate plant design from these principles. Chapters are devoted to chemical works pumping, distillations, extraction, drying, mixing, filtration, size reduction, and other facets.

Chemical Engineering Techniques. by R. E. Lauer and Russel F. Heckman. *Reinhold Publishing Corp.*, $6.00, 406 pp., 1952.—The book provides a comprehensive assemblage of industrially proven methods for conducting chemical manufacturing operations. Basic procedure rather than specific equipment is emphasized. The book begins with fundamental operations such as transportation and storage. The main material is presented under four sections: Preparation of material for reaction; production and distribution of energy; conditions affecting the chemical reaction; and the separation and purification of materials. Sale, shipment, storage, or other use is also dealt with in the final section.

Handbook of Chemistry and Physics. *The Chemical Rubber Co.*, $7.50 (student price, $5.50), 33rd edition, 2857 pp., 1951 to 1952.—New tables, formulae, and analyses, formulated, computed, and tabulated by the 173 contributors to this standard work have been included in the latest edition. Among the new tables included in the edition are: atomic constants, atomic absorption coefficients for X-rays, emission spectra of the heavy elements—protactinium, neptunium, plutonium, and americium, and a table of powers of two for exponents from 1 to 100. Section one contains mathematical tables; section two, properties and physical constants; section three general chemical tables; section four, physics data; and section five, quantities and units.

Electronic Iron Core Preferred Dimensional Specifications. *Metal Powder Assn.*, 25c, 1952.—All of the types of electronic cores made from iron powder and commonly used by the radio and television industry have been listed. First released in 1950, the standard has been brought up to date. The standard defines the terms associated with electronic cores made from powdered magnetic materials and specifies the preferred dimensions of standard sizes and shapes. Dimensions are listed for plain iron cores, insert iron cores, threaded iron cores, tuning cores, and sleeve iron cores.

Mathematical Tables. *The Chemical Rubber Co.* $1.75 (desk size), $1.25 (pocket size), ninth edition. 396 pp., 1952.—Material and data in past editions have been expanded upon and additional material has been added. An extensive collection of mathematical abbreviations and symbols, a 15-page table of natural secants and cosecants for angles in degrees and minutes, and a small table for the conversion of angles from arc to time have been added. The book has been designed to provide quick easy reference. A six-page index covers 350 subjects.

Direct-Current Machinery, by Charles S. Siskind. *McGraw-Hill Book Co., Inc.* $6.00, 319 pp., 1952.—The reader must have an elementary knowledge of principles of electric and magnetic circuits. The subject matter progresses through the fundamental theories of generators and motor operation, the uses of auxiliary and control equipment, the numerous constructions and applications of present day dc machines and devices, and the development of special machines. The object is to provide a logical text for a one semester course.

Theory of Elasticity and Plasticity, by the late H. M. Westergaard. *Harvard University Press and John Wiley & Sons, Inc.* $5.00, 176 pp.—This third book in the Harvard Monographs in Applied Science, is an introduction to the theories of elasticity and plasticity by one of the workers in the field who has made significant contributions to it. It is written from the point of view of the engineer although the treatment is entirely theoretical. An important feature is a historical chapter, which serves as a natural means of introducing many of the ideas that are later discussed in detail. Some of the topics covered include: Stress, strain, Hooke's law, the basic equation of elasticity, laws of plasticity, strain potential, hollow cylinders and spheres, inertia forces, thermal stresses, the Galerkin vector, and effects of a single force.

Mechanics of Materials, by Alvin Sloane. *The Macmillan Co.* $5.50, 468 pp.—In this textbook intended for the engineering student, the author attempts to express the fundamental theorems of mechanics of materials in a clear and direct manner. An integrated organization of the content is used to encourage logical thinking. For example, the predominant feature of the subject—the basic beam or flexure theory—is treated as a fundamental core. The theories of longitudinal shear and of deflection are corollary to this theory, and appear as correlated branches. Such factors as the theories of torsion, combined stress, and failure, follow. This pattern of coordination is followed throughout the book.

X-Ray Crystallographic Technology, by A. Guinier. *Hilger & Watts Ltd.* $9.50, 330 pp.—This work has been translated from the French by T. L. Tippell, and edited by K. Lonsdale. The book begins with the general properties of X-rays and their generation and goes on to the elements of crystallography and theory of X-ray diffraction of crystals. It also includes descriptions of experimental methods, applications of X-ray crystal analysis, crystal imperfections, amorphous substances, and determining the size of submicroscopic particles by low angle scattering. The appendices contain theoretical calculations upon which results reported in the book are based, and a number of useful tables. This book should be important as a handbook for those using X-ray diffraction methods in routine work and a comprehensive guide for all interested in the development of the subject.

Investment Castings for Engineers, by Rawson L. Wood and Davidlee Von Ludwig. *Reinhold Publishing Corp.* $10.00, 477 pp.—This comprehensive description of the features, advantages and limitations of investment castings as now employed in the metalworking industries should be of assistance to all technologists in the metal casting and related fields. Emphasis throughout is on design engineering factors which determine the attainable precision of cast dimension, cleanliness, and uniformity of metallurgical structure. Present design and metallurgical limits are defined, as are the degrees of cast tolerance control now commercially obtainable. All metallurgical data are derived from actual test results of investment cast specimens, and various interrelationships between wax, plastic and mercury processes are outlined. Recent techniques are described in detail, and the mechanics of the frozen mercury method are included.

A Source Book in Chemistry 1400-1900, by Henry M. Leicester and Herbert S. Klickstein. *McGraw-Hill Book Co., Inc.* $7.50, 554 pp.—Selections from 82 noteworthy papers in the history of chemistry, from Agricola to Madame Curie, are contained in this volume. Each paper is preceded by a brief introduction explaining the significance of the contribution and relating it to the other selections. The extracts dealing with metallurgy, combustion, electrochemical phenomena, and gas diffusion will be of particular interest to engineers.

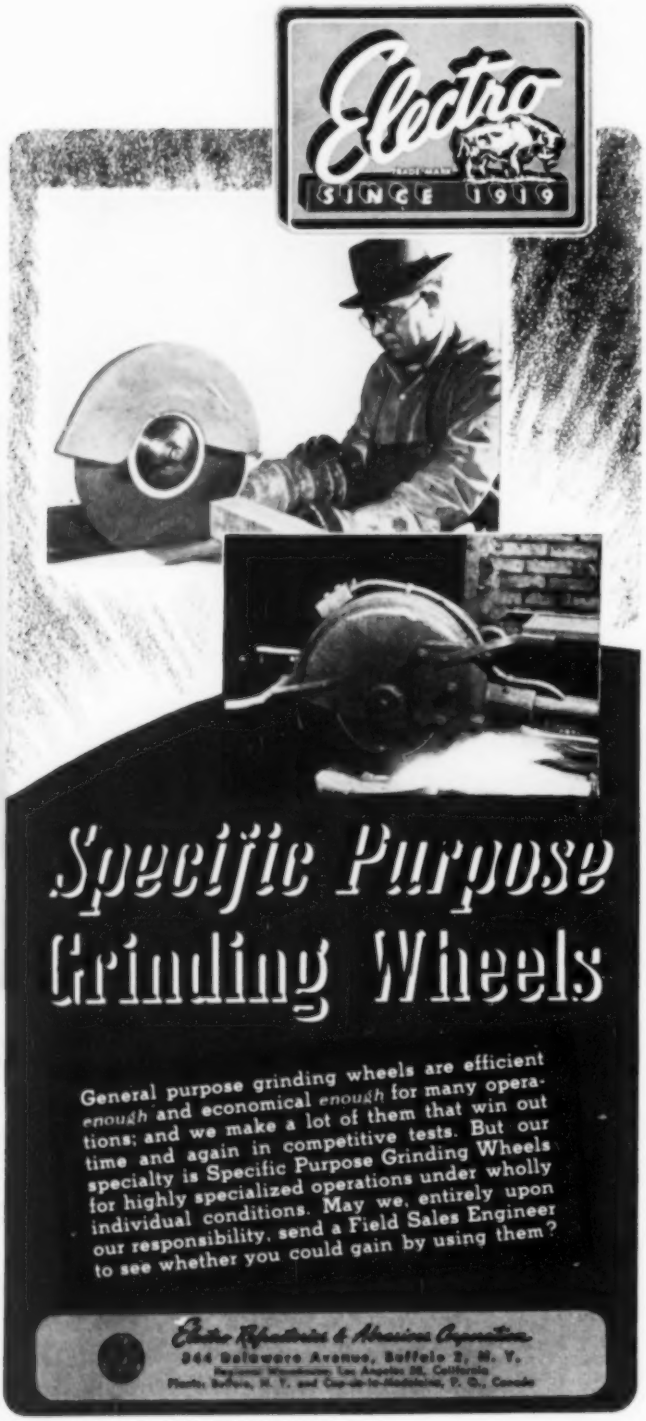
Steels in Modern Industry, edited by W. E. Benbow. *Iliffe & Sons, Ltd.* $9.00, 362 pp.—Part I of this compact reference work is a general metallurgical introduction covering the principal types of steel in relation to composition and heat treatment. Part II contains a series of general articles on the properties and characteristics of steels under the major operating conditions of stress, temperature, and environment encountered in service. Part III deals with selected and specific user aspects in the fields of structural, mechanical, and electrical engineering. In Part IV consideration is given to some of the more important forms of surface treatment. A selected list of references is appended to each article.

Proceedings of the First World Metallurgical Congress. *American Society for Metals.* $10.00, 835 pp.—Some 50 technical papers by American and foreign authorities are included in this volume, broadly classified under the following major subject divisions: Mining, melting, and refining; fabrication development and application of metals; mechanical metallurgy; surface metallurgy; physical metallurgy. The opening program and several introductory papers on metals for defense, metal reserves, and metal conservation are also included.

Metallurgical Engineering Volume I, by Reinhardt Schuhmann, Jr. *Addison-Wesley Press.* $7.50, 390 pp., 1952.—This first volume, engineering principles, of a two volume work, is intended by the author to meet a need for reorganization of instruction in extractive metallurgy. Its three main objectives are to organize the subject matter according to basic principles and unit processes; to integrate the underlying science of physical chemistry with metallurgical engineering; and to put greater emphasis in analysis and quantitative solution of engineering problems. Vol. I deals with unit processes, stoichiometry, thermodynamics, fuels, fluid flow, heat transfer, pyrometallurgical systems and refractories. Vol. II will take up the individual unit processes themselves.

Hydraulics and Its Application, fifth edition, by A. H. Gibson. *Constable & Co. Ltd.* London. 35s, 813 pp., 1952.—This textbook has been revised and new material added to provide up-to-date coverage. A new chapter deals with the basic principles of the construction and operation of scale models.

Fatigue and Fracture of Metals, edited by William M. Murray. *John Wiley & Sons, Inc.* and the *Technology Press.* $6.00, 313 pp.—The book is a record of a symposium held at the Massachusetts Institute of Technology, surveying general experience with failure of metals and certain specific fields in which it occurs. The book considers the internal mechanisms probably involved in fatigue damage, the significance of various metallurgical phenomena to fatigue, the potential usefulness of different research methods to disclose more about the mechanism behind the phenomenon itself, ways of countering it in design, and a forecast of the direction which research in the future may be expected to take.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Industrial Notes . .

• The Birmingham, England firm of Birlec, Ltd., an associate of Pittsburgh Lectromelt Furnace Corp., has been given an order for the largest electric arc melting furnace in Europe by Samuel Fox & Co., Ltd., Stockbridge. The furnace will have an annual output of about 75,000 tons of high quality alloy steel. It will produce about double the tonnage at each melting of the electric arc furnaces now in England. It will have a capacity 41 pct larger than any other electric furnace in Europe at the present time.

• **Stanford University business students have developed a new mold making process for metal casting. Big savings are promised for the small manufacturer. In place of ramming sand around a wood pattern to form a green sand mold, the process calls for a mixture of sand and thermosetting plastic to be brought into contact with a hot metal pattern. The hot pattern cures the adjacent sand, forming a thin rigid shell. Molten metal is poured into two such shells after they have been clamped together. The cost is said to be about 30 pct less.**

• *Chrysler Corp.'s Dodge forge plant in Detroit is turning out high quality automobile crankshafts by a continuous automatic press forging process. Productum is two to three times faster than by former methods. Three elements in the system are of outstanding significance. Primary is a 6000-ton forging press, capable of more than 35 strokes per min. A rotary, doughnut-type billet heating furnace, about 32 ft diam receives, heats, and discharges crankshaft billets automatically. The automatic heat treating and tempering furnaces handle crankshaft forgings suspended vertically throughout heating, quenching, and tempering. An elaborate system of electrical and hydraulic devices maintain the flow of materials.*

• The Longview, Wash. plant of Reynolds Aluminum Co., has increased its capacity from 60 million to 100 million lb of pig aluminum per year by enlargement of the plant's 372 reduction pots. The pot structures were moved individually to a Swan Island, Wash. firm for fabrication. They were cut in two and joining sections were welded in to expand them. All three of the reworked potlines are back in operation. The expansion increased the amount of electricity the Longview installation purchases from the Bonneville Administration from 66,000

to 100,000 kw. The expansion program started in February 1952. Production was maintained at 50 pct of normal despite handicaps.

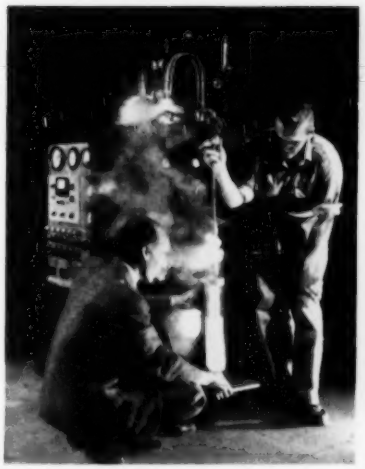
• *A new type of weather-resistant and maintenance-free modular panel of aluminum covered plywood is being used in the construction of Thule Air Base, Greenland, buildings. The development of an elastic glue line which expands and contracts with the metal has made the development possible. Previously, the difference between the coefficient of expansion of the two materials made their combined use impossible. The modular panels, known as armorply, make it possible for two men using large wrenches to erect a durable and sturdy hangar, barrack, or warehouse.*

• Goodyear Tire & Rubber Co. will be the operating contractor for the uranium-235 production plant to be built in Pike County, Ohio, according to the Atomic Energy Commission. The plant, will be erected at a cost of $1.2 billion. Goodyear will be the chief employer, with a force of about 4000 workers. The AEC said Goodyear will cooperate with Union Carbide & Carbon Corp., operating contractor for the gaseous diffusion plants at Oak Ridge, Tenn., and Paducah, Ky. The Pike County plant will use gaseous diffusion products for production of fissionable materials.

• **Canadian ferrous and nonferrous metal companies can expect demands for wage increases during the next two years from the Canadian Steel Workers Union. Plans to campaign for an average 20c per hr increase for about 53,000 members of the 70,000 member union were announced by C. H. Millard, Canadian director of the United Steel Workers, CIO-Canadian Congress of Labor. Canadian steel workers recently won an increase which made the basic wage $1.43½ an hr, the same as in the U. S. Millard said he hoped to gain increases for the other workers in ferrous and nonferrous plants.**

• A 15-ton capacity unloader being constructed by the Dravo Corp., will handle unloading of imported iron ore for Tennessee Coal & Iron Div. of U. S. Steel Co., at its new iron ore terminal in Mobile, Ala. The unloader will operate on four eight-wheel trucks along the dock of a slip in the Mobile River. Ore will be deposited into hoppers feeding a 42-in. wide conveyor belt.

RESEARCH *in* METALS



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The physical properties of metals have never been extensively investigated at temperatures below 80°K. In general, most metals become stronger and more brittle as the temperature is lowered but their behavior is unpredictable. For example, ordinary steel shows an unexpected transition from brittle to elastic fracture at about 60°K—and steel is not unique. Much needs to be learned.

Continuous measurements on a given sample over the complete temperature range from ambient to 4°K are now possible with the ADL Collins Helium Cryostat. This automatic helium liquefier has provided leading laboratories throughout the world with the temperatures necessary to study without thermal disturbance the phenomena of electrical resistance, specific heat, magnetic susceptibility, thermal conductivity, etc.

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Anti-ferromagnetism
Determination of ferromagnetic impurities

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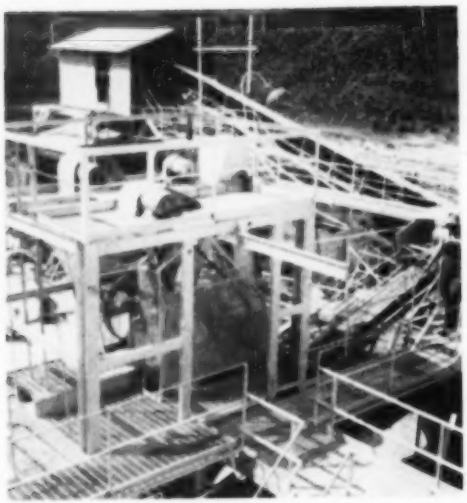
RESEARCH · TECHNICAL ECONOMICS · ENGINEERING · ADVANCED EQUIPMENT



The Colorado plateau has been the scene of an almost huge, spectacular growth. Uranium mines are spread throughout the area, and production of the vital mineral is being stepped up throughout the region. Typical of the development is this processing mill, where each load of uranium ore brought to Uravan by truck is carried by conveyors through precise sampling equipment.

UNITED States Vanadium Co. has placed a new uranium treatment process in operation at the Uravan, Colo. mill, which may open the doors to use of heretofore uneconomical uranium ores. High lime ores are fairly abundant in the Colorado Plateau area, but the presence of lime added to the difficulty and cost of extracting the uranium. It is hoped that the new installations will overcome the problems previously encountered.

The Uravan mill is the largest uranium ore treatment mill in the nation. Capacity has been doubled as the result of an expansion program begun August 1951. Presently, there are eight mills processing uranium ore in the Colorado Plateau area. Two mills are under construction. The new facilities at the Uravan mill provide additional capacity equal to, or in some cases surpassing that of any of the mills operating in the area.

The enlarged facilities involved erection of several thickening and solution tanks of approximately 40,000-gal capacity, new roasters several stories high, additional filtering equipment, and enlargement of the sampling plant. It has been estimated that about $30 million is being spent in developing the Colorado Plateau. It has become the second largest uranium source in the world, with more than 5000 people involved in this part of the atomic energy program.

More than 200 mines are in operation on the plateau, many of them small operations with a working force of only a few men. One of the greatest problems to be overcome in the area is transportation. Many of the roads are no wider than old wagon trails. The AEC is sponsoring a $4 million road building program, with over $2 million being spent in Colorado.

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WHEN foreign visitors come to the U. S. they see a country whose strength arises from its bigness, geographically, and industrially. What they often miss, and Americans often fail to see, are the many small producers engaged in the tremendous display of strength and industrial accomplishment.

Today, steel is undergoing the greatest expansion program the world has ever seen. Its strides are seven league, and production, despite the steel strike, is one of the miracles of the century. But almost unnoticed, the smaller steel plants have set a pace which in proportion dwarfs the efforts of the big companies. The plans of 25 of the smaller companies show an expected increase of 50 pct in two years, from the start of their programs in 1951 to the beginning of 1953. As a group, the 25 companies accounted for 5.1 pct of the national total capacity in 1951, and they will have 6.8 pct next year. In addition, a wider diversification of finished steel products is anticipated, if plans proceed according to schedule. They have between 175 and 3900 employees.

One company, when plans are completed, will have increased its steelmaking capacity by 200 pct over 1940, and two others will have gained 93 and 95 pct respectively. Another company will complete an expansion program of about 70 pct in 13 years. Four companies made no steel at all in 1940, but when plans are finished they will be producing 870,000 tons by the first of next year.

Here are some of the highlights in the plans of several of the small companies:

◄ Build a new electric furnace capable of making 90,000 tons of steel annually. Enlarge facilities for manufacture of light structural shapes, hot rolled, strip steel, bars and wire rods. A scheduled rise of steel capacity of 48 pct between 1951 and 1953. Rise in hot rolled finishing capacity by 32 pct.

◄ Increase coke oven capacity, build new blast furnace, increase open hearth capacity. A hot rolled strip mill expected to make 900,000 tons of hot rolled strip in coils, add cold rolled strip mill. The capacity of hot rolled finished products to rise 189 pct between 1951 and 1953.

◄ Build steelmaking capacity for use in making tubular steel products, add two-high slabbing mill and pipe finishing mills. Steel capacity and hot finishing capacity to rise 100 pct between 1951 and 1953.

◄ Increase steel ingot capacity to match potential capacity of rolling mill equipment already installed. Increase soaking pit capacity. Increase hot rolled sheet steel capacity. Raise steel capacity 28 pct, hot rolled finished product capacity 6 pct between 1951 and 1953.

◄ Double capacity for open hearth steel. Increase capacity for making strip for black plate and tin plate. Steel capacity to rise 93 pct. Increase hot rolled finished product capacity 40 pct between 1951 and 1953.

The new National Steel Corp. blast furnace at its Zug Island (River Rouge, Mich.) blast furnace

div. plant increased the steel production capacity considerably of the Great Lakes Steel Corp., a subsidiary of National. The furnace is capable of producing 480,000 tons per year, and will raise Great Lakes annual ingot steel capacity by 580,000 tons to 3,150,000 tons. National is aiming at a 6 million ton a year capacity by 1953. Another unit of National, Weirton Steel Co., Weirton, W. Va., is putting a 480,000 ton per year furnace in operation.

The new Great Lakes furnace is equipped for high pressure blowing, which calls for about five times the normal gas pressure at the top, according to Julius Clauss, vice-president in charge of engineering at Great Lakes. A new ore dock has been built in connection with the furnace with a capacity of 450,000 tons of ore. A steam generating plant, power and blower house, water, steam, and air service lines sewers, pig casting machine, railway track system, first aid station, shops and other facilities were also installed with the furnace.

Other projects will complement the capacity raising program. A new battery of 70 coke ovens, a 45x90 in. slabbing mill and two additional 25-ton bessemer converters are also on the way. Great Lakes is expected to have a capacity of 3.5 million ingot tons by 1954.

National steel has been adding to its reserves of raw materials, with a large interest in two Pittsburgh district coal mines. It also has interests in the new Labrador iron ore fields.

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A NEW electric furnace, the first of three, has been installed at the Timken Roller Bearing Co. as part of its multi-million dollar steel and tube div. expansion program. The new furnace will increase production from 550,000 to 625,000 tons. Outstanding in the design of the new furnace is the electric stirrer. Higher quality steel is expected from the device which replaces manual stirring by the melter. A magnetic field is set up by rotating electromagnets underneath the furnace. The magnetic field, moving through the molten steel in the furnace, thoroughly stirs and mixes the heat. According to Timken, the new stirrer saves time and increases output, improves the quality and cleanliness of steel, and provides reliable temperature control and rapid sampling is possible by improving slag conditions of the heat. The first description of inductive stirring in arc furnaces appeared in JOURNAL OF METALS, January and February 1950.

The new furnace will be charged from the top by an overhead crane. It will consume about 550 kw of electricity per ton and produce approximately 14 to 16 tons per hr, contrasted to the 8½ ton per hr capacity of the old open hearth furnace it replaces. A 20,000 kva transformer controls the electric current. The furnace was constructed by the American Bridge Co. and installed by the Hunter Construction Co., of Youngstown, Ohio. The furnace, plus a full load of molten steel will amount to about 400 tons. The electric stirrer weighs about 25 tons. A water cooling system was installed as a safeguard for the stirrer. Thirty four thermocouples control water flow. The thermocouples automatically increase the flow of water when needed. They also activate an alarm when the temperature becomes unsafe.

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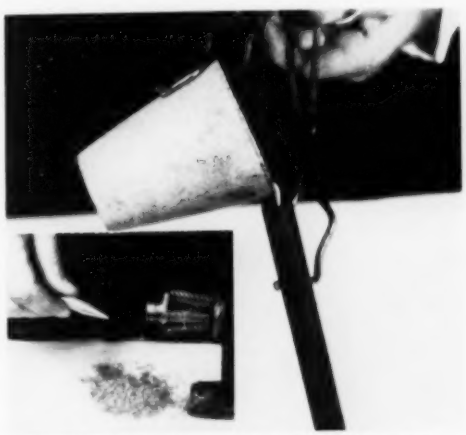
IT was generally accepted that the Defense Production Administration would announce a third-round aluminum production increase. The only surprise was the goal. DPA wants to increase production by 200,000 tons per year. The idea of the advanced production goal is that in the event of an all out war, U. S. aluminum requirements would be between 2.25 and 2.50 million tons. With third-round requirements filled, total capacity would be 1.7 million tons, not too far from full mobilization needs. Much of the needed new capacity may come from independent producers. Companies building new facilities to expand capacity will be entitled to fast tax amortization. Firm proposals were invited by defense mobilizer Henry Fowler. Samuel Anderson, deputy administrator for aluminum, made it quite plain that attempts will be made to obtain increased production from domestic sources.

DPA has been trying to get the expansion program since last March, but ran into considerable opposition from the big three aluminum producers and from the Congressional Watch Dog Committee in its move to sign a long range contract with Aluminum Co. of Canada. The Committee ordered the DPA to obtain additional production domestically.

The final motivation for the announcement of the new goal is the recently boosted Munitions Board stockpile requirements.



The U. S. Bureau of Mines at College Park, Md., is using an ordinary pencil sharpener to obtain small samples of soft metals for metallurgical analysis. Molten metal is poured from a crucible into a graphite mold for cooling. The mold's interior is the same size as an ordinary writing pencil. The hardened metal is drawn from the mold. In the insert it is being shredded by the pencil sharpener. The method has been used successfully on zinc, zinc aluminum, tin lead, lead zinc, and aluminum copper alloys.

Chapman Casts World's Largest Stainless Gate Valve

9-ton casting produced in austenitic chromium-nickel stainless steel

This valve, produced by The Chapman Valve Manufacturing Co., Indian Orchard, Mass., for the defense effort, is used in corrosive water service. It is stated to be the world's largest, with an overall height of 19 feet, weighing approximately 18,000 pounds. The rough casting weight was approximately 36,000 pounds.

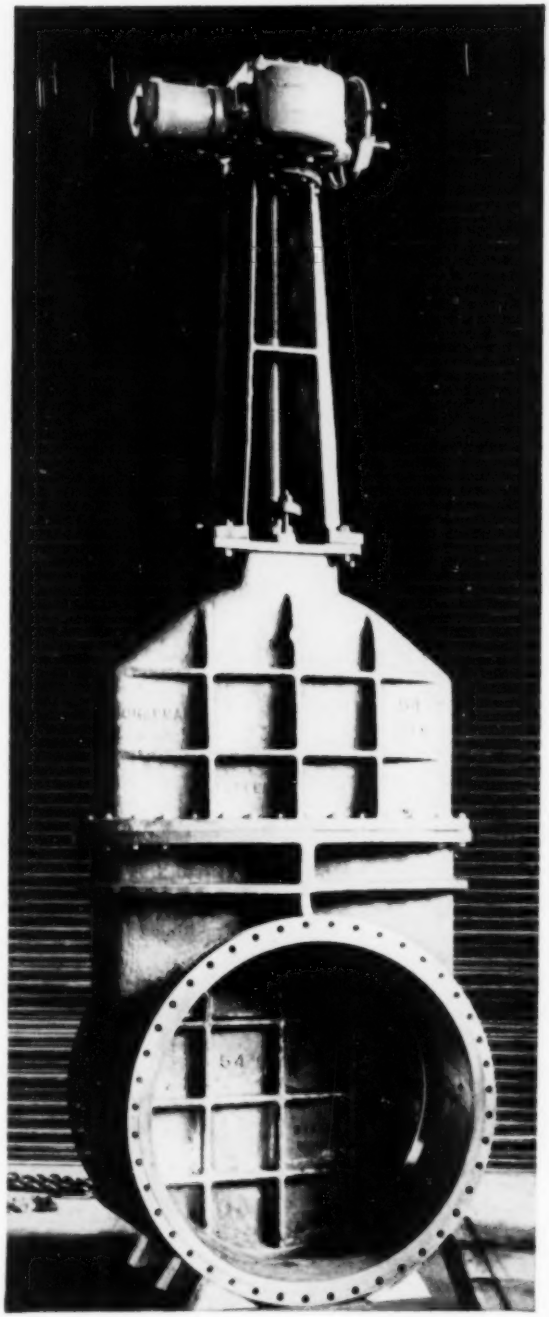
Cast in low carbon 18-8 chromium-nickel stainless steel, it is one more demonstration that size is no limiting factor when you cast parts in stainless steels to provide resistance to corrosion and erosion.

Stainless steel resists attack by nearly all oxidizing acid conditions. In addition, it helps you trim bulk and deadweight without sacrificing strength and safety.

At elevated temperatures, austenitic chromium-nickel stainless steels are distinguished by their strength and outstanding resistance to oxidation. At temperatures down to —320° F. they retain their toughness and unusual strength.

Investigate all the benefits stainless steels can give you. Leading stainless steel companies and foundries produce nickel-containing stainless steels in all commercial forms. A list of sources of supply will be furnished on request.

At the present time, the bulk of the nickel produced is being diverted to defense. Through application to the appropriate authorities, nickel is obtainable for the production of austenitic stainless steels for many end uses in defense and defense supporting industries.



INCO

THE INTERNATIONAL NICKEL COMPANY, INC. 67 WALL STREET NEW YORK 5, N. Y.

Anaconda Aluminum Co., new subsidiary of Anaconda Copper Co., will build its $45 million aluminum reduction plant at the foot of Teakettle Mountain, near Columbia Falls, Mont. The plant will have a capacity of 50,000 tons per year. Preliminary construction began in September, and completion is expected early in 1954.

A new gas washing unit is in operation at U. S. Steel's American Steel & Wire div., Donora, Pa., in cooperation with western Pennsylvania's smoke prevention campaign. In addition to promoting cleaner air, the gas cleaner will collect usable raw materials which eventually will be returned to the blast furnace in the form of sinter.

Manganese Chemical Co. will build a $2 million processing plant for the recovery of manganese from low grade Cuyuna range deposits in Minnesota. At least 200 tons of manganiferous iron ores will be treated daily. It is reported that they will use a chemical leaching process, the ammonium carbamate or Dean process. Manganese Chemical has done experimental work on the Dean process for which it has acquired patent rights.

Construction has started on National Carbon Co.'s $3,456,000 addition to its Columbia, Tenn. plant. The Union Carbide & Carbon Corp. subsidiary will produce graphite electrodes used in electric furnaces in the new plant. The company's manufacturing capacity will be increased about one third.

A new method for bonding ferrous and nonferrous metals to each other or to almost any nonmetallic material is available through an agreement between ChemoTec div. of Eutectic Welding Alloys Corp. and Ciba Co., Inc. The process will give high strength bonds at low heat in cases where welding, brazing or soldering proves impractical.

The Nation's first plant for the cold extrusion of steel for civilian use will be constructed by Mullins Mfg. Corp. at Warren, Ohio, at a cost of $2.6 million. The new plant will be part of Mullins' main facilities at Warren. To date, Mullins has used its Koldlfo process for making artillery shells. New equipment will make it possible for the company to cold extrude steel products up to 30 in. in length and weighing 50 lb.

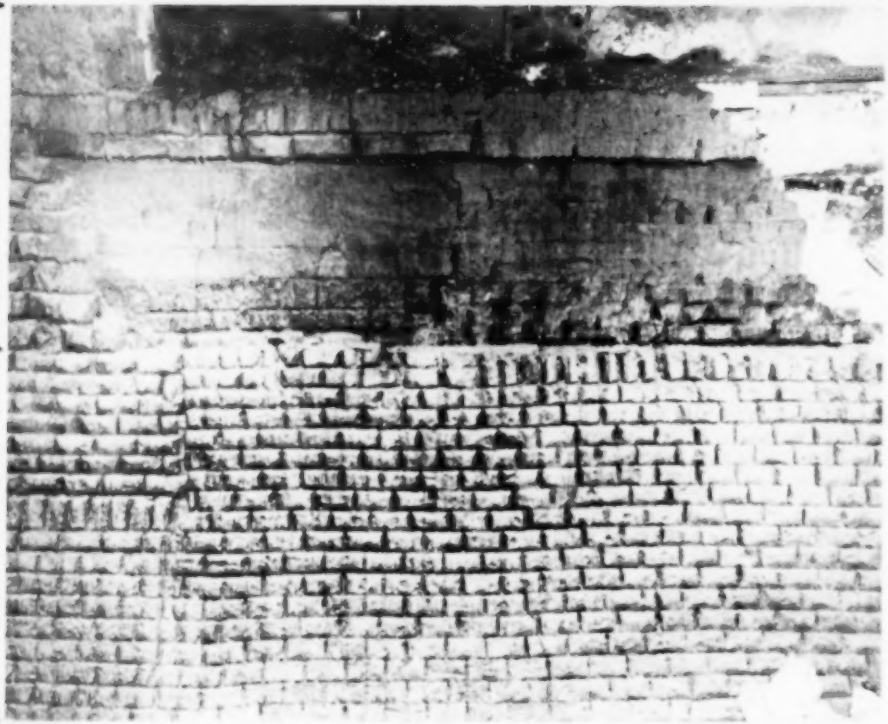
Battelle Memorial Institute announced development of a photoelectric scanner to be used for detection of flaws on ordnance, railway, aviation, and automotive equipment production lines. The device was developed in conjunction with the Magnaflux Corp., Chicago.

Molten metals can be treated safely with highly active additions such as sodium and magnesium by using a new injector cartridge. Developed by J.S.W. Bates, Phoenix, Ariz., the cartridge is made of the same base metal as the molten bath. A time fuse releases the additive gradually below the bath's surface.

TASIL IS TAYLOR-MADE FOR MIXERS!

high duty fireclay brick

TASIL brick and cement



TASIL LASTS TWO CAMPAIGNS

THE FIRST CAMPAIGN: Taylor Sillimanite (TASIL) brick laid in TASIL No. 302 Heat-Setting Cement was used to strengthen the vulnerable areas of the lining of a 1400 ton Hot Metal Mixer which began operation in June, 1950. In April, 1951, after approximately 450,000 tons had been through the mixer, the TASIL brick in the front and backwall were in such excellent condition—having lost only 2 to 2½ inches—that they were left in for a second campaign, while most sections of fireclay brick had to be replaced.

THE SECOND CAMPAIGN: From April to December, 1951. Handled approximately 377,000 additional tons. Condition of TASIL at end of *two* campaigns is shown in lower half of the above photograph.

TOTAL FOR TWO CAMPAIGNS: *18 months service, approximately 827,000 tons handled.*

This contrasts with a five-campaign average of 225,000 tons for Blast Furnace Quality Firebrick linings in this mixer.

Results such as this continue to prove that TASIL "Balanced" linings are unsurpassed, from the standpoint of over-all life and economy. Use TASIL Brick in the areas of severe erosion—fireclay or super-duty brick in the remainder of the lining—*all* laid in TASIL Cement. Call in a Taylor representative for a factual discussion of TASIL possibilities in your mixers, ladles and hot metal cars.

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REFRACTORIES ENGINEERING AND SUPPLIES, LTD.
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The CHAS. TAYLOR SONS Co.
A SUBSIDIARY OF NATIONAL LEAD COMPANY

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THE DRIFT OF THINGS

by Edward H. Robie

Round Trip to Spokane

SEPTEMBER usually being a fine month for motoring, we set out with our better half at the end of August in our Studebaker for points West. A combined business trip and vacation. The first night found us 392 miles away, at the Statler Hotel in Buffalo, and the next morning we revisited Niagara Falls for the first time in some forty years. The cataracts were as impressive as ever and certainly worth a day of any vacationist's time, instead of the half hour we could spare before going on to Chicago.

The Centennial of Engineering, the hundredth anniversary of the founding of the ASCE, no doubt attracted the greatest gathering of engineers in history but still the attendance was disappointing to most of the forty or fifty societies that participated. Perhaps the time—the two weeks following Labor Day—was unfavorable. Few could afford to spend ten days away from home and business at that time of the year. Fall meetings of the AIME normally attract far more than the 300 that registered in Chicago. The technical program, however, was excellent, especially that arranged by the Minerals Beneficiation and Industrial Minerals Divs. The mineral industry papers of a more general nature that were presented as a part of the Centennial program on Monday and Tuesday of the following week were of high quality and offered by top names but had a meager audience.

Undoubtedly the celebration brought engineers and engineering to the attention of millions of people. The pagent at the Museum of Science and Industry proved continuously interesting, showing the progress of engineering following the first use of fire. The show continued for many weeks. A special stamp was issued by the Government, which engineers might well use on their Christmas cards or other mail this year.

After six days in Chicago we set out north, first visiting Fairbanks Morse in Beloit and Allis-Chalmers in Milwaukee. Will Mitchell's Basic Industries Research Laboratory is doing interesting work and being installed in more comfortable quarters. The next day at Ishpeming, C. W. Allen arranged for luncheon with a local group of AIME members and we then looked over the new surface plant of the Mather B mine, a model of modern functional design. Then on to a small dinner meeting at Calumet following cocktails at Endicott Lovell's attractive summer home on the lake at Point Mills. The new Memorial Union Bldg. at Houghton, where we were domiciled for the night through the courtesy of Roy Drier, is a beautiful modern addition to the college, a model of its kind.

Lunch the next day in Duluth with a school-day friend, Walter Maxson, who is directing Oliver Iron's taconite research, and then on to Virginia for an evening meeting of the Minnesota Section's Minerals Beneficiation group. An attendance of 85 testified to the success of the Minnesota Section's plan of bringing the AIME to local members on a divisional basis. A mining group is similarly active. Each holds about four meetings a year, these supplementing the annual meeting of the Section in mid-January in Duluth. The next morning was spent in revisiting some of the big iron pits on the Mesabi Range with Bill Taylor and C. J. Calvin, and then on to Grand Forks, N. D.

Grand Forks has a fine new Bureau of Mines building, to be devoted to fuel technology, and of course the University of North Dakota. A mining curriculum is well established, as is an AIME Student Chapter. Such well-known MBD'ers as Grover Holt and Joe Swainson graduated there. By nightfall the next day we were at Williston, where who should we run into but Charley and Eda Millikan, who the next morning showed us over Amerada's wells in the new and famous Williston basin thereby considerably increasing our knowledge of petroleum production. That afternoon we saw the Fort Peck dam, the biggest earth fill dam in the world, some four miles long and about a mile wide at one point. Later we saw the Hungry Horse dam in Idaho under construction, the fourth biggest concrete dam in the world. In between we drove through Glacier Park on the famed Going-to-the-Sun Highway, perhaps as beautiful a mountain ride as there is in the country.

High spots of the next week started with a luncheon meeting with Columbia Section officers at Spokane. Incidentally, Spokane has a beautiful new modern hotel, the Ridpath, which we can recommend. Then on to Wallace for a dinner meeting with some of the Coeur d'Alene Subsection members. The next morning, a trip around the district and a visit to AS&R's new Galena mine. Lunch at the attractive new Florence Hotel at Missoula, and a never-to-be forgotten dinner with Chester Steele and other Montana Section notables that night at Teddy Trepartsch's Rocky Mountain Cafe at Meaderville. No gambling left there but plenty of good food and drink. A little sightseeing the next morning on "the richest hill on earth" and in the afternoon into Yellowstone Park. A page or two could be devoted here to the pitfalls of visiting national parks after the season has closed.

The next day a trip of over 400 miles through Wyoming, winding up with a dinner meeting with a Wyoming Section group at Laramie, at the Diamond Horseshoe no less. And Saturday night down at Denver a fine meeting of the Colorado Section.

Then six days at the Mining Congress meeting, perhaps the biggest aggregation of mining men ever held, with a fine machinery show. It started Sunday afternoon with a trip to Golden to see all the new buildings and equipment at Colorado's world-famous mining school; and wound up, for us, on Friday with a trip to the famous mining district of a half century ago —Cripple Creek. This included a mountain trout luncheon at the Elks Club in Victor, underground in the Ajax mine, and a steak dinner at the famous Broadmoor in Colorado Springs. There is nothing like a mining field trip to establish friendships which often prove lasting.

Denver to Chicago took the better part of three days. Here the trip was punctuated by a flight down to Houston for the Petroleum Branch fall meeting. More than 1500 men and close to 400 ladies registered, the Branch's biggest meeting ever. An earnest, young, live and friendly group who have contributed a great deal to the progress of the Institute in the last few years. A fine buffet supper and water show at Glenn McCarthy's famous Shamrock.

And finally home. No accidents of any kind, nor did we even see one. Practically perfect weather, warm and only a couple hours of rain in five weeks. Some 6700 miles covered, at 20.7 miles per gal actual mileage, 5 pct less than the speedometer reading, most speedometers, including ours, being fast. Western highways excellent, and faster than in the East, but the Pennsylvania Turnpike, now 325 miles long, the finest of all. A memorable trip. We are more than ever proud of our profession and our country.

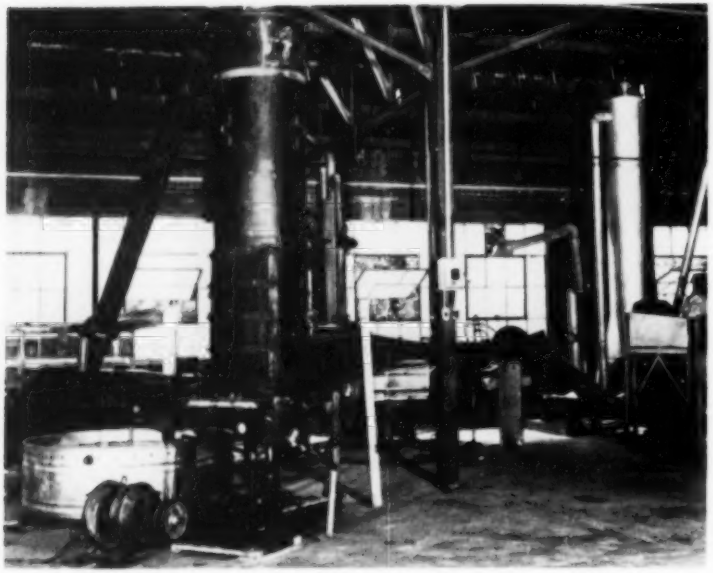

Fig. 1 — Elaborate fume and vapor recovery devices are essential in studying the potential utilization of new germanium sources. The pilot plant shown is smelting germaniferous ores.

Germanium, Produced As a Byproduct, Has Become of Primary Importance

Most of the production of germanium in the U. S. is from byproducts of smelting Tri-State zinc ore. Only in England has commercial manufacture of germanium been reported as a byproduct of the burning of coal.

by A. P. Thompson and J. R. Musgrave

GERMANIUM, predicted by Newlands[1] and Mendeleeff,[2] discovered by Winkler[3] and studied for years from a chemical standpoint, had to await the advance of science before it could be put to work for the benefit of humanity. Although small quantities of germanium and many of its compounds were prepared and several uses suggested for them, it was not until the fundamentals of solid state physics were developed that much attention was paid to germanium.

It is increasingly true that scientists use a *library* approach in their search for certain properties. They list the properties desired for a certain material and then inspect the entire field for such a material. In the course of developing crystal rectifiers during World War II, the National Defense Research Council wanted a material or materials with semiconducting properties that could be made of high purity and handled easily. Of the materials selected, pure germanium proved one of the most adaptable and the commercial manufacture and use of germanium really dates from this work. The rapidly advancing achievements in the field of semiconductors and their utilization in numerous applications have made germanium an important element, although the amount produced is small compared to many other elements.

A. P. THOMPSON is Director of Research and J. R. MUSGRAVE is associated with the Eagle Picher Co., Joplin, Mo.

Early History

Many years before the advent of solid state physics, university workers investigated germanium

and its compounds, but the metal was only a scientific curiosity. As is often the case with such rare elements, it sold for $10 per g. The presence of germanium in Tri-State (Missouri-Oklahoma-Kansas) ores was known prior to 1920; Waring[1] publicly identified it, although other scientists in that area also studied its occurrence there. In 1935, McCutcheon showed that germanium was concentrated in certain byproducts of the zinc smelting operation at the Eagle-Picher plant in Henryetta, Okla. and, after considerable study, was successful in further concentrating the germanium. Additional studies, both at Henryetta and in the Eagle-Picher research laboratories in Joplin, Mo., resulted in pilot plant scale production of germanium dioxide about 1941. At that time, no commercial uses were known.

About 1942, the National Defense Research Council began work on germanium.[2] The pilot plant was then producing GeO_2 of 99.9 pct purity which, although good, was not pure enough for rectifier purposes. Continuous cooperation between producer and consumers improved the purity until today the total impurities are only a few parts per million, while the electronically important impurities are normally in fractions of parts per million.

The rapid rise in the use of germanium during the past few years is a remarkable tribute to the group effort of participating units. The tenacity and courage of the group which first made germanium available commercially should be extolled, but the development of high-purity germanium and its electronic uses is attributed to the unremitting work of the producers, university and commercial research scientists, theoretical physicists and electronic engineers who have cooperated closely to achieve the desired results.

Occurrence

Germanium occurs in the earth's crust in the same order as zinc and lead. It has been estimated that 4 to 7 g of germanium are present in each ton of lithosphere.[3,4] However, unlike zinc and lead, there is very little concentration of germanium which allows economic exploitation. No minerals are known in which germanium is the primary constituent, although in germanite and renierite it is a secondary metal. Some germanite has been found in the copper-lead mines at Tsumeb, South West Africa; the run-of-mine ore assays 3 to 4 pct Ge. The occurrence of germanite is reported to be erratic, but such ore as is available is used as a raw material for germanium recovery. Renierite, found in the Belgian Congo, is reported to be available in sufficient quantity to make it commercially attractive.[5]

Some silver, tin, copper, zinc, and iron ores contain small amounts of germanium, 0.01 to 0.1 pct. These traces cannot be economically recovered from the ore, but in some cases germanium can be recovered as a byproduct during the recovery of the primary metals. Most of the U. S. production of germanium is from byproducts of zinc smelting (from Tri-State ore). Germanium is found in coals from many parts of the world. Under proper conditions of combustion, germanium is retained in the ashes or other byproducts of the burning. Exploitation of this source is dependent on sufficient amounts of germanium in these byproducts to allow economic recovery. Only in England has commercial manufacture of germanium been reported from this source.[6] Some American coals have been investigated for germanium[7] but no utilization of coal byproducts in the U. S. has been reported.

Table I. Physical Constants of Germanium

Atomic Number		32
Atomic weight		72.59
Isotopes and Abundance[8]	Mass No. 70, pct	20.4
	Mass No. 72, pct	27.4
	Mass No. 73, pct	7.8
	Mass No. 74, pct	36.6
	Mass No. 76, pct	7.8
Color		Silvery
Crystal Structure[9]		Octahedral
Index of Refraction[10]		4.068-4.143
Hardness,[10] Mohs Scale (a)		6.25
Ductility		Frangible
Density[11] (a) 25°C, g per cc		5.32
Specific Volume (a) 25°C		0.0188
Melting Point,[12] °C		958.5
Boiling Point,[13] °C, approx.		2700
Latent Heat of Fusion,[14] g cal per g		114.3
Latent Heat of Vaporization,[15] g cal per g, approx.		1650
Specific Heat[16] at 25°C, cal per g		0.086
Volume Resistivity[17] at 25°C, microhm-cm		60 x 10^6
Electrochemical Equivalent[18] Ge^{++}, mg per coulomb		0.1881
Electrode Potential,[19] $Ge^{++} + H_2 \rightleftharpoons 0.0$ v.,* estimated		0.15

* National Bureau of Standards nomenclature.

Properties

Germanium is usually considered as a metalloid, with properties somewhere between those of a true metal and a nonmetal. It belongs to the class of materials known as semiconductors; these semiconducting properties have led to its increasing use in electronics. Germanium is both divalent and tetravalent; the latter compounds are the more stable. Physical constants of germanium metal are summarized in Table I.

The metal is quite stable at 25°C. It is not affected by air, water or oxygen. At 600° to 700°C, oxidation in air or oxygen proceeds rapidly.[20] Germanium combines readily with the halogens upon heating to form the corresponding tetrahalides. Chlorine reacts most vigorously, followed by bromine and iodine.

Hydrochloric and sulphuric acids have little effect on germanium at room temperature, but at 100°C sulphuric acid will dissolve germanium slowly. Both nitric acid and aqua regia will attack germanium, especially at higher temperatures. Potassium or sodium hydroxide solutions have little or no effect on germanium, but the molten alkalies quickly dissolve the metal. Germanium forms two oxides—GeO and GeO_2. The latter, germanium dioxide, is the type sold commercially.

Johnson[21] has summarized the extensive work done on organo-metallic compounds of germanium.

Germanium or germanium dioxide shows no evidence of toxicity.[22] Germanium tetrachloride is irritating when inhaled; this is believed to result from the hydrolysis of the compounds to GeO_2 and HCl. The released acid is probably the cause of irritation.

Recovery

Each raw material for germanium recovery poses its own set of problems in extractive metallurgy. A pilot plant smelting germaniferous ores is shown in Fig. 1. Flow sheets for the three present sources—zinc ore, Fig. 2; germanite, Figs. 3 and 4; and coal, Fig. 5, are shown. While they vary considerably, each produces a crude germanium tetrachloride for final purification. A flow sheet for the translation of crude tetrachloride to purified metal is presented in Fig. 6.

In the recovery from zinc sulphide ores,[23] the zinc sulphide containing 0.01 to 0.015 pct Ge is first roasted. The roasted ore is mixed with coal and salt and sintered at a high temperature. Germanium,

cadmium, lead, and some other metallic impurities are volatilized and the vapors condensed and collected in an electrostatic precipitator. This fume is reacted with sulphuric acid and the lead precipitated as lead sulphate. Zinc dust is then added in sufficient amounts to precipitate the copper and germanium without throwing down the cadmium. Some arsenic and other metals are also precipitated at this stage. The copper-germanium precipitate is filtered off and the solution is sent to the cadmium recovery unit. The germanium-bearing sludge is redissolved and the germanium concentrated by a second precipitation. This germanium concentrate is then roasted and the roasted concentrate dissolved in strong hydrochloric acid. Germanium tetrachloride, along with some hydrochloric acid and arsenic chloride, is distilled from this solution. This is the crude tetrachloride charged for purification.

Large quantities of British coals are used to make coke for producer gas plants. In the combustion of producer gas, germanium is largely volatilized. Upon cooling of the combustion gases, much of the germanium, and some other metallic constituents, are deposited as a dust in the flues. This flue dust is smelted with soda ash, lime, copper oxide, and coal dust (iron is also desirable, but is usually present in sufficient quantity in the dust) to form a regulus and a slag.[5] Under proper smelting conditions, the regulus will contain most of the germanium and the gallium. The regulus is then treated with a current of chlorine under a dilute solution of ferric chloride, the gallium and germanium being converted to soluble chlorides. The germanium tetrachloride so formed is distilled off and collected, along with some arsenic chloride. This crude tetrachloride is then further purified.

Flow Sheets of Processes Producing Crude Germanium Tetrachloride

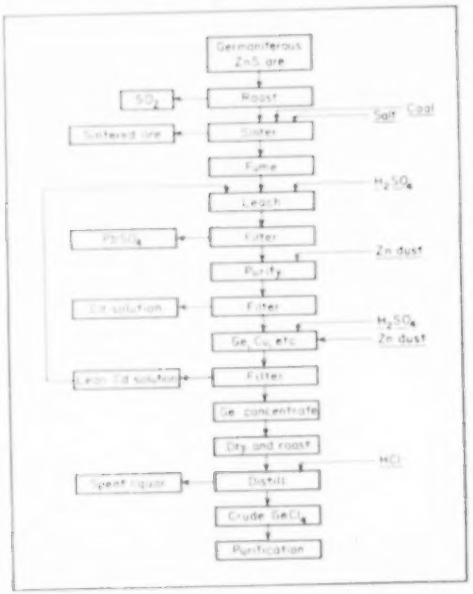

Fig. 2—This illustrates U. S. practice utilizing zinc ores, and accounts for most of the germanium production here.

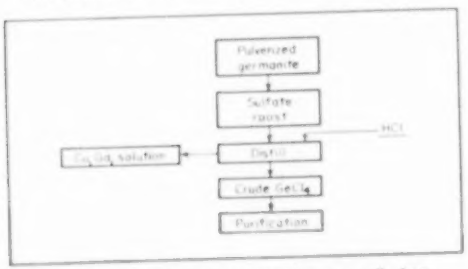

Fig. 3—Some germanium is recovered commercially from germanite in this U. S. process. It differs somewhat from the British practice shown in Fig. 4.

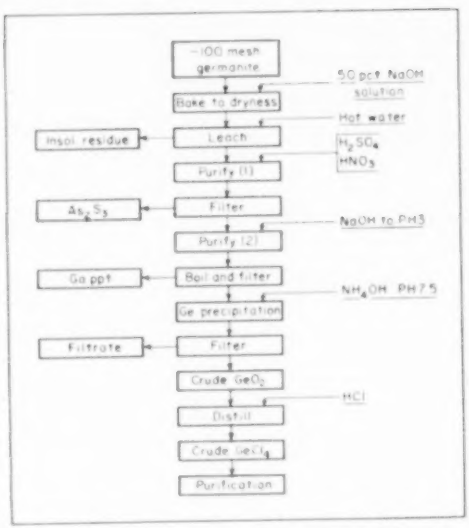

Fig. 4—This British germanite practice is somewhat more complicated than the U. S. process utilizing the same ore.

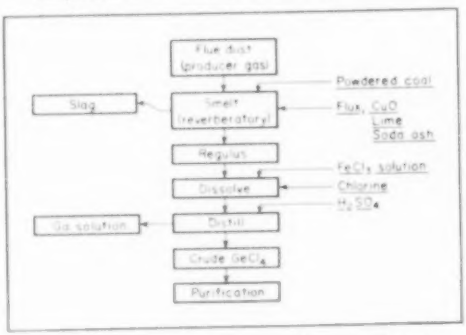

Fig. 5—Only in England has commercial success been reported on the production of germanium from flue dust. American coals are being investigated for germanium.

Germanium has been recovered commercially from germanite in both England and the U. S. The processes differ somewhat. In the British method the pulverized germanite ore is reacted with 50 pct sodium hydroxide solution and the mixture evaporated to dryness. The dry mass is leached with hot water and the leach solution brought to pH 8 with sulphuric acid. Under controlled conditions, nitric acid is added to the boiling solution to give 5 pct of free acid in the solution; after filtering, this solution is brought to pH 3 with sodium hydroxide to precipitate the gallium. The gallium precipitate is filtered off and the germanium precipitated (as dioxide) by neutralization with ammonia. The germanium dioxide is then filtered from the solution, dissolved in strong hydrochloric acid and the resultant crude germanium tetrachloride distilled. In the American process, however, the ore is pulverized and then roasted under controlled conditions, after which it is reacted directly with hydrochloric acid. Germanium tetrachloride is distilled from this hydrochloric acid solution and the crude tetrachloride sent to the purification process.

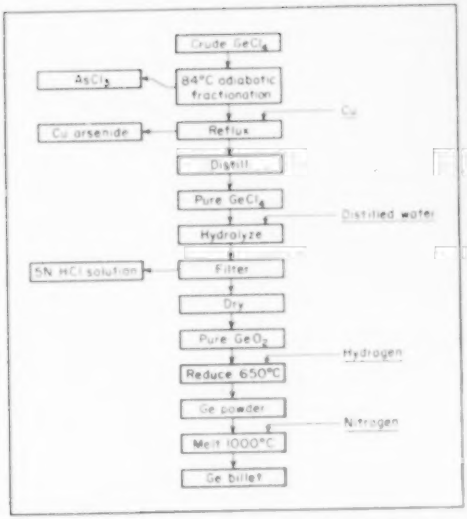

Fig. 6—Germanium tetrachloride is purified in this British process, hydrolized to germanium dioxide, and the dioxide reduced. The American process for purifying the tetrachloride differs only slightly in that adiabatic columns are not used, and the copper refluxing step is omitted.

Purification

In the purification of the crude tetrachloride, the American method[7] employs multiple distillation of the crude germanium tetrachloride, either as a batch or column process, with the final distillations being conducted in the presence of chlorine and hydrochloric acid. Primary distillation is carried out as shown in Fig. 7. The British process[8] is much similar, except that adiabatic columns are used and an additional step of refluxing with copper is employed to eliminate arsenic. The pure germanium tetrachloride from either process is hydrolyzed in distilled water to germanium dioxide, which is then washed and dried. Scrupulous cleanliness is essential at all stages to insure no contamination of the

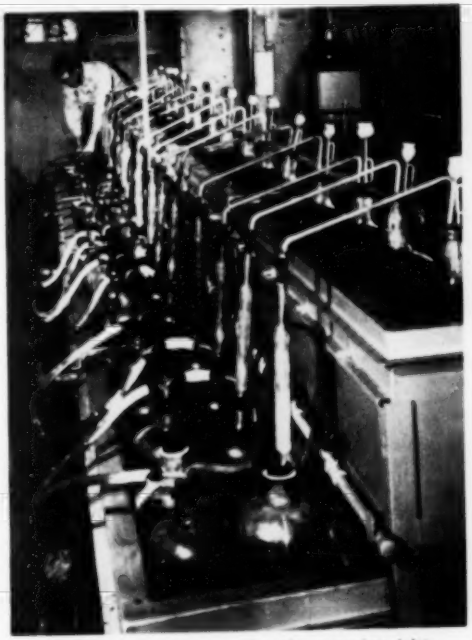

Fig. 7—Primary distillation of crude germanium tetrachloride from hydrochloric acid solution is carried out in the apparatus shown.

final product. The germanium dioxide is reduced to a powdered metal by heating to 650° C in an atmosphere of hydrogen. The powdered metal is melted at 1100° C in an inert atmosphere to form billets. Fig. 8 shows an enlarged section of germanium billets.

For electronic uses, germanium metal is further purified by fractional recrystallization.[9] The metal, contained in a graphite boat, is melted in a horizontal tube furnace at 1000° C, either in an inert atmosphere or under vacuum. Upon slowly cooling the molten metal from one end to the other, the impurities concentrate at the two ends of the ingot, leaving the center section relatively pure. Additional recrystallizations of the center sections may be necessary to achieve the desired purity. Thermal treatment of germanium billets is shown in Fig. 9.

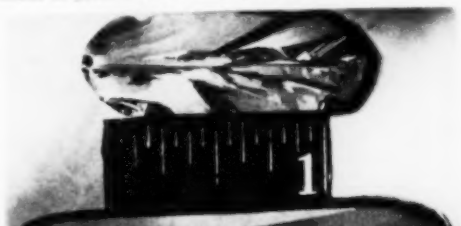

Fig. 8—Germanium is melted into billets as shown in this enlarged view. The upper billet is multicrystalline, while the lower billet has only two crystals. The demarcation line of crystals can be seen.

Fig. 9—Various thermal treatments of germanium billets are required to develop maximum utility in electronic use. The exact treatment depends on the end use.

In preparation of germanium for electronic devices, several different techniques are used.[9] Single crystals of germanium are produced by *seeding* a melt of germanium (held only slightly above the melting point) and slowly withdrawing the crystal from the furnace. Other methods of producing types of germanium for such uses are pressure, heating and quenching, or alloying with minute amounts of other metals. Many alloys have been patented for these purposes.[7, 8] Alloying is usually done in an inert atmosphere or under vacuum.

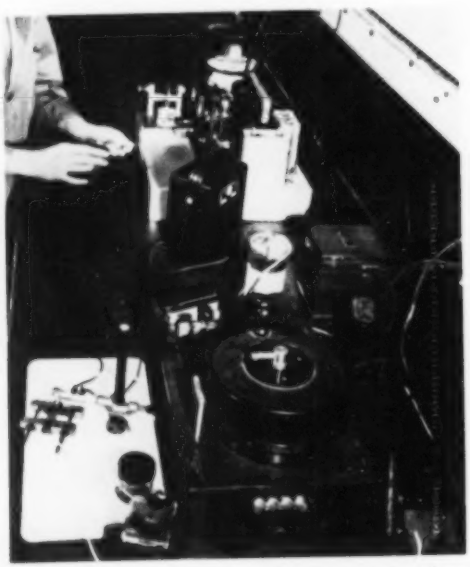

Fig. 10—Careful testing of the electronic properties of germanium is necessary. Proper preparation of the metal, and the fabrication of the electronic devices constitute a major portion of the cost.

Commercial production of germanium dioxide was begun about 1941 by the Eagle-Picher Co. Demand was limited until the development of the germanium diode for use as a crystal rectifier. By 1948, the production of germanium dioxide had reached 1000 lb per year in the U. S.[7] Since that time, demand has increased until, in 1951, it was estimated that 5000 to 6000 lb were produced.[9] The Eagle-Picher Co. is the dominant producer, recovering it from zinc ore. In 1950, Johnson, Matthey & Co. began production in England from flue dusts (coal). Some germanium is produced on the continent, but no data are available on quantities from either Europe or England. The price of germanium metal in the U. S. is currently $340 per lb; the dioxide sells for $142 per lb. Small quantities are somewhat higher.

Uses

The high cost of germanium is no deterrent to its use in most electronic devices, since the quantity necessary is quite small. For example, a germanium diode, which currently sells for about $1.25, contains only a few cents worth of germanium. Proper preparation of the metal and the fabrication of the devices constitute a major portion of the cost. Fig. 10 illustrates the testing of germanium for electronic properties.

The first type of germanium devices to achieve commercial importance was the germanium diode, which is essentially a fine wire of appropriate metal pressing against a thin wafer of properly prepared germanium. Both wire and wafer are soldered to electric conductors and a suitable covering provided. The complete assembly is only the size of a grain of corn. The two-element unit acts as a crystal rectifier and, within the limitations of the unit, will perform the same functions as a vacuum tube diode. Besides its advantage in size, it is far more rugged and consumes only a very small amount of power (and gives off very little heat) compared to the vacuum tube. In addition, it begins functioning at once, while the vacuum tube must await heating of the filament. Because of these advantages, it is possible to use germanium diodes in many places to

replace vacuum tubes, giving more compact and serviceable units. These germanium diodes are being produced at an estimated rate of seven to eight million per year.[49] Size and shape of germanium diodes and triodes can be seen in Fig. 11.

Germanium triodes, known as transistors, were invented by Bardeen and Brattian of the Bell Telephone Laboratories in 1948.[50] The first transistors had much the same appearance as did the germanium diodes, except that two wires made contact with the germanium wafer instead of one. More recently a different type, made of a single tiny block of germanium so treated that the center section has different properties than the two end sections, has been built. The earlier type is called a point-contact transistor, the newer type a junction (or area) transistor. Each kind has its own peculiar advantages and limitations.[51]

Transistors have distinct advantages over the vacuum tube triodes in much the same manner as do the germanium diodes over the vacuum tube. Particularly in communication equipment, computers and many other electronic uses, the small size and greater dependability of the transistors allows major improvements in design and performance. When it is known that many of the failures in such types of equipment are caused by vacuum tube failures, the importance of the long-lived transistor (its life has been estimated at 10 years) can be realized.

Transistors are presently in the *pilot plant* stage; large scale production awaits development of mass-production techniques. As more transistors become available, new uses are found for them.

The photoelectric effect of germanium diodes, first observed during the development of crystal rectifiers,[52] has been carried to commercial utilization in photoelectric devices. They are said to have definite advantages over the present *electric eyes*.

Germanium rectifiers that will operate in the ranges of selenium and copper oxide rectifiers are in the development stage.[53] Some magnesium germanate is used as a phosphor in fluorescent lamps.[54] Germanium is transparent to infrared light and this property may be utilized in special optical units. Glasses, where all or part of the silicon dioxide has been replaced with germanium dioxide, may have utility because of the high index of refraction and high dispersion of the germanium glasses.

Many alloys of germanium have been investigated, but only a few have found commercial utilization. Gold-germanium alloys have been suggested for use in dental work or precision casting[55] because of their expansion on solidification. The low melting gold-germanium eutectic could be used as an improved gold solder or in reduction of melting temperature of gold-containing alloys.

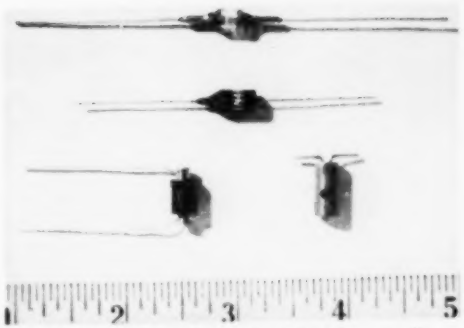

Fig. 11—These germanium diodes and triodes are quite small, averaging about 1 in. long (less wires). In the lower right hand corner, one of the first point contact transistors can be seen. The other devices are commercial diodes.

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Small Additions Raise Strength Of Zirconium at Elevated Temperatures

Small additions of molybdenum and niobium (columbium) to induction melted zirconium resulted in increased strength at temperatures below 500°C. Aluminum, tantalum, and vanadium additions were most effective in maintaining strength over 600°C. Titanium was the most effective addition to zirconium in the 300° to 700°C range.

by A. D. Schwope and W. Chubb

IN this age of extreme temperatures and pressures, the strength of a material at elevated temperatures is an important consideration. For this reason the effect of minor additions upon the strength of zirconium in the range from room temperature to 800°C was studied. Preliminary work on the properties of zirconium alloys has been done[1] by the Bureau of Mines[2] and by the Foote Mineral Co.[3] The alloys prepared in the present investigation were selected on the basis of the results of these preliminary studies, and were compounded on the basis of the expected solubility of the additive element in zirconium. The solubilities were determined from phase diagrams when available or estimated, using Hume-Rothery rules.

The alloys used were prepared by induction melting in outgassed graphite crucibles. The zirconium used was Foote Mineral Co. iodide zirconium, and the minor alloying elements used were of high purity. The charge was added to the crucible and melted in two stages to minimize overheating. When completely fused, the charge was cooled slowly in the melting crucible. This procedure introduced approximately 0.3 pct carbon and some oxygen and nitrogen into all alloys. The alloys were melted in an absolute pressure of less than 10 microns of mercury with the exception of alloys containing lead and zinc. These alloys were melted under an atmosphere of purified argon.

The ingots weighing approximately 200 g were forged and rolled at 1000°C in air to ⅛-in. sheet; cold rolled (whenever possible) to 0.070 in.; and annealed in a straightening press in a vacuum furnace for 1 to 3 hr at 700°C. The resulting sheet was cleaned, as necessary, by machining up to 0.010 in. off each side. Tensile specimens cut from this sheet were approximately 3 in. long and ⅜ in. wide. The reduced section was 1½ in. long and approximately 7/16 in. wide. Specimens were taken parallel to the rolling direction.

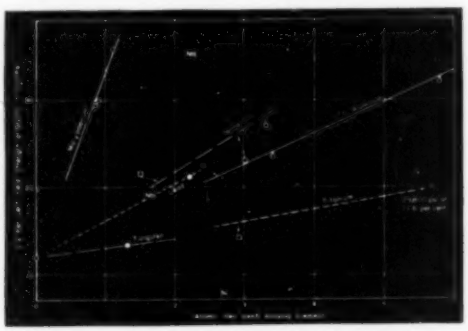

Fig. 1—It is apparent from this plot of yield strength vs atomic percent that molybdenum and possibly niobium (columbium) are more effective in strengthening zirconium than most other elements.

Experimental Procedure

Chemical analyses were made on samples taken after the ingots were reduced to sheet form.

Tensile tests were run at 500°C using a 20,000-lb Baldwin-Southwark universal testing machine. The sheet tensile specimens were mounted in grips inside a tubular resistance furnace. The ends of the furnace were loosely closed with asbestos fiber, and argon gas was passed into the annular space around the specimen. The temperature of the specimen was measured by means of two thermocouples located

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near the ends of the gage section. The speed of travel of the head of the testing machine was 0.02 ipm. An extensometer with a 1-in. gage length and an accuracy of ±0.0001 in. per in. was used to measure extensions. This extensometer was of the clip-on type utilizing SR-4 gages with slide bars extending out of the heated area around the specimen. The test temperature was selected as being above the recrystallization temperature of unalloyed zirconium, so that effects of alloying elements upon the strength of zirconium in this range could be determined.

Diamond pyramid hardnesses of some of the alloys were obtained at elevated temperatures by means of a vacuum hot-hardness machine. This device is the same machine as that described by P. S. Bergh,[1] and is similar to the machine used by F. P. Bens[2] except that the vacuum chamber contains a stationary diamond indenter mounted over a hydraulically operated ceramic stage. The indenter, specimen, and stage are heated by open-wire heating coils immediately surrounding them. A thermocouple mounted in the center of the ceramic stage records the temperature of the specimen, and an indexing device enables the operator to move the specimen across the stage.

In a typical run, five indentations were made at room temperature, 204°, 316°, and 427°C; four indentations at 482° and 538°C; and three indentations at 649°, 704°, 760°, and 816°C. A load of 500 g was applied by means of the hydraulic stage for approximately 15 sec. When a run was complete, the specimen was cooled to room temperature and the indentations measured. The resulting values were averaged for each temperature and a corresponding diamond pyramid hardness number calculated.

Table I. Mechanical Properties of Zirconium Alloys at 500°C

Zirconium Alloy*		Strength, 1000 Psi		Elong. in 1 in. Pct	Reduct. Area Pct
Atomic Pct	Weight Pct	0.2 Pct Yield	Ultimate Tensile		
Induction Melted Zr		11.2	21.5	45	55
Induction Melted Zr		16.0	24.0	30	44
Induction Melted Zr		9.0	15.0	71	63
1.2 Al	0.38 Al	18.6	30.0	31	34
2.4 Al	0.82 Al	22.4	34.7	49	57
2.5 Al	0.87 Al	25.0	38.0	30	37
3.4 Al	1.2 Al	21.5	37.5	14	41
5.8 Al	2.0 Al	32.0	46.1	25	38
2.2 Pb	4.7 Pb	21.2	31.0	31	39
0.78 Mo	0.82 Mo	14.5	24.3	52	62
0.85 Mo	0.90 Mo	25.9	42.5	27	60
0.85 Mo	0.90 Mo	30.0	43.5	21	54
1.1 Mo	1.2 Mo	35.8	48.0	44	56
2.7 Ni	1.8 Ni	7.8	14.4	82	64
1.6 Nb	1.6 Nb	19.2	28.9	59	77
2.2 Nb	2.2 Nb	35.0	43.0	9	15
1.5 Ta	3.0 Ta	21.5	28.0	21	32
3.0 Ta	5.9 Ta	23.0	32.0	36	53
3.3 Ta	6.4 Ta	27.0	32.8	24	46
2.0 Ti	1.6 Ti	14.2	28.6	31	48
11.6 Ti	6.4 Ti	29.8	42.4	19	28
14.5 Ti	8.0 Ti	29.0	45.0	30	43
19 Ti	10.4 Ti	41.2	58.3	33	44
0.22 W	0.44 W	16.7	22.0	47	65
0.23 W	0.45 W	10.4	16.0	26	56
1.3 W	2.6 W	13.3	19.1	50	56
5.3 V	3.1 V	27.7	34.6	40	60
5.5 V	3.2 V	21.6	35.0	44	73
0.55 Zn	0.40 Zn	12.0	23.2	47	46
2.9 Mo + 0.4 Nb	3.1 Mo + 0.4 Nb	32.0	39.0	12	16
8.2 Ti + 2.6 Al	4.6 Ti + 0.8 Al	32.0	46.8	23	34
7.1 Ti + 1.8 Mo	3.9 Ti + 1.9 Mo	47.6	52.5	20	57
7.3 Ti + 1.2 N	4.0 Ti + 0.2 N	34.0	49.0	18	24

* These alloys also contain approximately 0.3 pct carbon.

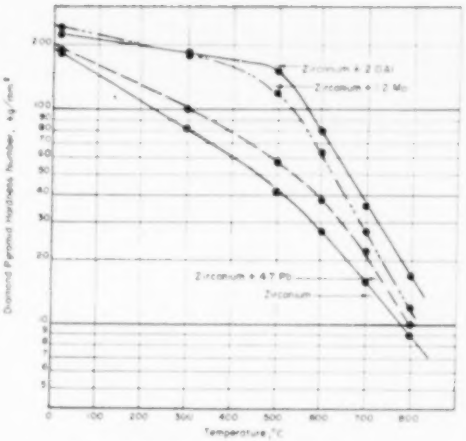

Fig. 2—The hot hardness curves for alloys of zirconium with aluminum, molybdenum, and lead are shown. Molybdenum does not maintain the strength of zirconium above 600°C, while aluminum seems to be most effective above 600°C.

Microstructures of all alloys were examined in the annealed condition. The specimens were mounted in bakelite, polished by hand, and etched with a solution containing approximately 5 pct ammonium bifluoride and 2 pct ammonium persulphate. Repolishing and re-etching usually were necessary to remove disturbed metal, and to establish the proper time of etching.

Results and Discussion

In most cases duplicate tensile tests were run on each alloy at 500°C. The results of these tests were averaged and appear in Table I. When the yield-strength data in Table I were plotted against atomic percent, Fig. 1 was obtained. Lines were drawn on Fig. 1 to indicate trends whenever the data seem to

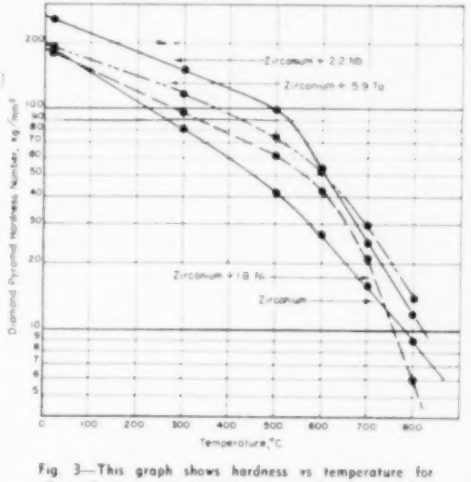

Fig. 3—This graph shows hardness vs temperature for alloys of zirconium with niobium, tantalum, and nickel. Tantalum is most effective above 600°C, while the effect of niobium falls off at that temperature.

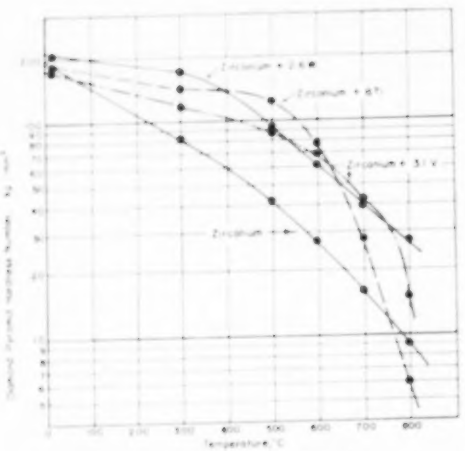

Fig. 4—In these hot hardness curves for alloys of zirconium with tungsten, titanium, and vanadium, the curve for the tungsten alloy must be disregarded for comparison. The carbides present in this alloy increase hardness but do not correspondingly increase strength.

show such trends. Isolated points are shown by the chemical symbol of the alloying element. It is apparent that molybdenum and possibly niobium (columbium) are more effective in strengthening zirconium at 500° C than most other elements. Probably this result will be traced to the lower transformation temperatures and more sluggish diffusion rates of zirconium alloys containing molybdenum and niobium.

The hot-hardness curves for some of the alloys are shown in Fig. 2, 3, 4, and 5. The hot-hardness curve for the 2.6 pct tungsten alloy is shown in Fig. 4, but this curve must be disregarded for comparison purposes, since the finely dispersed carbides present in this alloy contribute unduly to its hardness without appreciably increasing its strength.

These curves must be used with caution since it

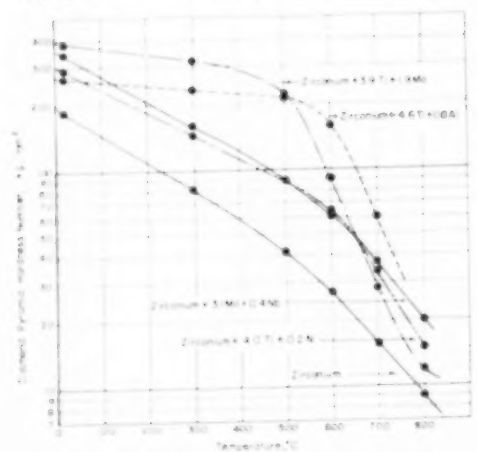

Fig. 5—The behavior of ternary alloys of zirconium can be seen in these hot hardness curves. The Zr-Ti-Mo alloy loses hardness and strength above 500° C, while the Zr-Ti-Al alloy has highest hardness above 500° C.

probably is improper to convert directly from hardness to strength. However, the curves are useful in that they enable the tensile strength of a particular alloy to be estimated for temperatures other than the test temperature. As such, the shapes of the hot-hardness curves show which alloying elements tend to strengthen zirconium at low temperatures and which tend to strengthen at high temperatures.

These data show that while molybdenum and niobium are very effective up to about 500° C, they do not maintain the strength of zirconium very well above 600° C. Titanium seems to have a very pronounced effect upon the strength of zirconium in the range 300° to 700° C. Aluminum, tantalum, and vanadium seem to be most effective above 600° C. The results of combining these effects are shown by the behavior of the ternary alloys. The combination of titanium and molybdenum produces an alloy that is extremely hard and strong up to about 500° C, but which rapidly loses hardness and strength above this temperature. The combination of titanium and aluminum produces an alloy with considerably lower hardness at room temperature, approximately the same hardness at 500° C, and much higher hardness at 700° C than the titanium-molybdenum ternary alloy.

Examination of the microstructures of the alloys revealed the presence of carbides in all alloys. These carbides appeared as rather large elliptical particles arranged in rows corresponding to the rolling direction, with the exception of the carbides in the tungsten alloys. The carbides in the tungsten alloys were finely dispersed, and probably represent the results of complex carbide formation. No other phases were detected in the titanium, tantalum, niobium, lead, and zinc binary alloys. The aluminum and molybdenum binary alloys and all the ternary alloys contained small particles of an additional phase. The nickel and vanadium alloys were definitely eutectoid in character.

Conclusion

The effects of small amounts of a number of elements upon the strength of zirconium have been studied. The results agree in general with the data available in the literature, and show the effects of small additions upon the high-temperature strength of induction-melted zirconium. It is apparent that molybdenum and possibly niobium are most effective in strengthening zirconium at temperatures below 500° C, but that aluminum, tantalum, and vanadium are most effective in maintaining the strength of zirconium at temperatures above 600° C. Titanium seems to be most effective in the range between 300° and 700° C. This work was performed under AEC Contract No. W-7405-eng-92.

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The Paley Report:

Manganese

HIGH GRADE manganese ore, from which manganese is obtained commercially, is not found in large quantities in any major steel producing nation in the free world. The U. S. is a "have not" nation with respect to deposits of directly mineable high grade manganese ore. Known resources of 48 pct Mn or better grade ore amount to less than 200,000 tons.

In 1950 the U. S. steel industry consumed 1.8 million short tons of metallurgical grade manganese ore that contained about 800,000 tons of manganese. About 16 pct of the manganese content was lost in processing, so that about 650,000 tons, or 13 lb per ton of steel actually entered into steel production. Under present practices use expands directly with steel output, and by 1975 the demand in both the U. S. and the rest of the free world is expected to be roughly 60 pct greater than in 1950.

In peacetime about 80 pct of manganese consumption goes into steel production: high-manganese steel, dry cells, and chemicals account for the remainder.

The manganese supply problem centers around high grade ore for ferromanganese production. Use of ores containing less than 35 pct Mn sharply increases the costs of making ferromanganese. Use of ferromanganese of grade below 70 pct in turn requires changes in steelmaking that increase steel cost.

Under normal conditions the present small domestic production cannot be expected to increase. Major resources in the U. S. consist of 12 low grade deposits. The cost of mining and treating these ores to extract a product as good as that yielded by imported ores is at least twice and in some cases more than four times the 1951 price of foreign ores delivered to the U. S.

However, as long as trade relations and overseas shipping are not interrupted, deposits in India, Africa, and Brazil can meet steadily increasing demand at approximately present costs.

Cost considerations indicate that the U. S. should continue to rely upon overseas sources for its peacetime supply, and that this situation is satisfactory. But, this does not take into account the question of how the U. S. will be able to meet its needs in war.

Position of the Rest of the Free World

In 1950, free world steel producers outside the U. S., with a steel output of 70 million ingot tons, consumed about 1.3 million tons of metallurgical-grade ore. Their manganese ore demand, expected to increase directly with steel production, will by 1975 be about 2.3 million tons.

Russia possesses over half the known manganese ore reserves of the world and is producing twice the tonnage of any other country. It supplied more than a third of the U. S. manganese requirements up to 1938 and again in 1948, but by 1950 Soviet manganese exports to the free world had virtually ceased. The free world's supply of manganese now comes mainly from India and Africa. Somewhat over 10 pct of U. S. imports came from Brazil and Cuba.

Security Considerations

In the event of war the U. S. might be substantially cut off from 90 pct of present sources.

Reduction in manganese specifications might cut consumption by over 10 pct without seriously affecting steel quality. By elimination of losses in the production of ferromanganese savings as high as 10 pct might be possible. But, wartime manganese requirements cannot be met through conservation alone.

To meet possible future emergencies the U. S. should continue its comprehensive security program for manganese, including stockpiling and research on the economic use of low grade ore, domestic ores, the recovery of manganese from slag and the reduction of manganese requirements in steel production. If this work, including additional pilot plant operation is pursued vigorously, it should be possible in an emergency to get an adequate supply of manganese from domestic sources. The national stockpile then can be looked upon as a source of supply during the period of at least 2 years required to reach full-scale production from low grade resources.

Ferromanganese Smelting

In comparison with smelting of pig iron, ferromanganese smelting is a very wasteful process. Under present ferromanganese blast furnace smelting practice, about 8 pct of the manganese in the furnace charge is lost to the slag, and roughly the same amount is lost to the stack gases; the total loss approaches 15 pct.

Present practice is a compromise between excessive slag loss and excessive stack loss. In fact, it may be seriously questioned whether conventional blast furnace design is suitable for manganese smelting.

U. S. Resources

The known manganese deposits of the U. S. contain a total of 3500 million long tons of raw material

and 7.5 million long tons of metallic manganese. More than 90 pct of this contained metal is in 12 large low grade deposits of which the most important are those at Chamberlain, S. D., Cuyuna, Minn., Aroostook County, Maine, and Artillery Peak, Ariz.

Reserves of high grade ore (48 pct Mn) amount to less than 200,000 tons. About 20 million tons of ore average over 15 pct Mn, and when grade is decreased to 10 pct Mn reserves amount to about 100 million long tons. If cut-off grade is decreased to 5 pct Mn, resources amount to 800 million long tons. Many of these low grade ores may be beneficiated by flotation or other concentration methods.

Pyrometallurgical Methods

For smelting ferromanganese, it is essential to have an ore containing at least 50 pct manganese, with an Mn Fe ratio of about 8:1. Direct smelting of 20 pct Mn concentrates is not promising. The only method that offers any promise involves two-step smelting. Concentrate would be smelted in a blast furnace to produce pig iron and a slag containing over 50 pct Mn. The second step would produce standard 80 pct ferromanganese from this slag.

Four patents by Royster deal with a two-step blast-furnace treatment for low grade ores. Cost of ferromanganese has been estimated as about $80 above cost of ore used, 10 tons of ore being required per ton of ferromanganese.

Chemical Methods

No appreciable quantity of ferromanganese or metal is produced from domestic ores by chemical processes today, except a small amount produced electrolytically by Electromanganese Corp. at Knoxville, Tenn. Electrolytic recovery of manganese is believed to be limited to applications requiring pure manganese regardless of cost.

However, several of the presently known chemical techniques are almost competitive economically, and large-scale plants could be built immediately on the basis of present knowledge if foreign supply were cut off or prices rose.

In 1943 the Manganese Ore Co. opened a plant at the Three Kids, Nev., deposit to produce 300 tons per day of MnO by the sulphur dioxide process. The plant closed after a year because of high costs and availability of foreign ore supply.

(Manganese, Inc., is building a 1200 ton per day plant to treat Three Kids ore, using flotation to produce ~48 pct Mn concentrate.)

The Chemico process appears to be a practical development of the sulphur dioxide method. Chemical Construction Co. estimates that a plant to produce 60 pct oxide equivalent to 200 tons of manganese per day, treating Cuyuna concentrates, would cost $12 million. Cost of manganese, without credit for by-product iron, would be $1.23 per long ton unit, compared to current quotations of $1.20 for foreign ores.

Ammonia methods include the Bradley-Fitch and Dean processes. The Dean method appears more feasible. Detailed cost estimates are not available, but Manganese Chemicals, Inc., Minneapolis, Minn. has acquired the Dean patents and is carrying out experimental work.

(DMPA has recently granted a loan to Manganese Chemical Corp. for a 200 ton per day plant.)

Recovery from Waste Products

Annual waste of metallic manganese in open hearth slags in the U. S. exceeds a million tons; more than the total requirements in the form of ferromanganese. One way to avoid this waste is to recover manganese from slags in the form of ferroalloys and another approach is based on the recovery of manganese from pig iron before it reaches the open hearth.

A three-step, pyrometallurgical method of manganese recovery from flush-off open hearth slags is being evaluated by the Bureau of Mines for the American Iron and Steel Institute in a pilot plant.

The first step utilizes extremely high blast temperatures (up to 3000 F), producing high phosphorous spiegel of 2 to 4 pct P and up to 20 pct Mn. In the second step the spiegel will be partially blown in a Bessemer converter producing high-manganese slag and iron suitable for the basic Bessemer process. The third step is production of standard 80 pct ferromanganese in a blast furnace from the high-manganese slag.

(Recent reports indicate the first two steps are a metallurgical success.)

Based on many assumptions, the manufacturing cost of ferromanganese by the Bureau of Mines process will possibly approach $300 per ton.

The Sylvester-Dean process also is being tried by the Bureau of Mines on flush-off slags.

Plan for Recovering Manganese from Iron

The suggested plan for reducing manganese waste and to expand the economic use of domestic manganiferous ores is based upon two important facts: 1—A manganese content above 0.5 to 0.8 pct in basic iron is not essential to good open hearth practice; and 2—desiliconization of molten iron, as a preliminary step to its use in the open hearth, speeds up furnace operation and lowers operating costs.

Desiliconization of iron by passing hot metal through an oxidation station would produce a slag which is essentially a manganese silicate. This iron-oxidation slag should lend itself readily to one of several treatments such as the Chemico process.

This suggested method could prove to be a source of more than half the estimated annual manganese requirements, and it would seem logical to augment this source by increasing quantities of native low-manganese ores in blast furnace burden.

An appraisal of the economics of the suggested process, using either the Chemico or the Sylvester-Dean treatment, and crediting the savings in operating cost due to the oxidation step, indicates a cost for standard 80 pct ferromanganese of roughly $100 per long ton, as compared to present price of $185.

Improved technology should tend toward making this country self-sufficient in manganese. Rather than decrease the use of manganese as a final addition to steel, future efforts should be devoted to decreasing the waste of manganese in steelmaking processes.

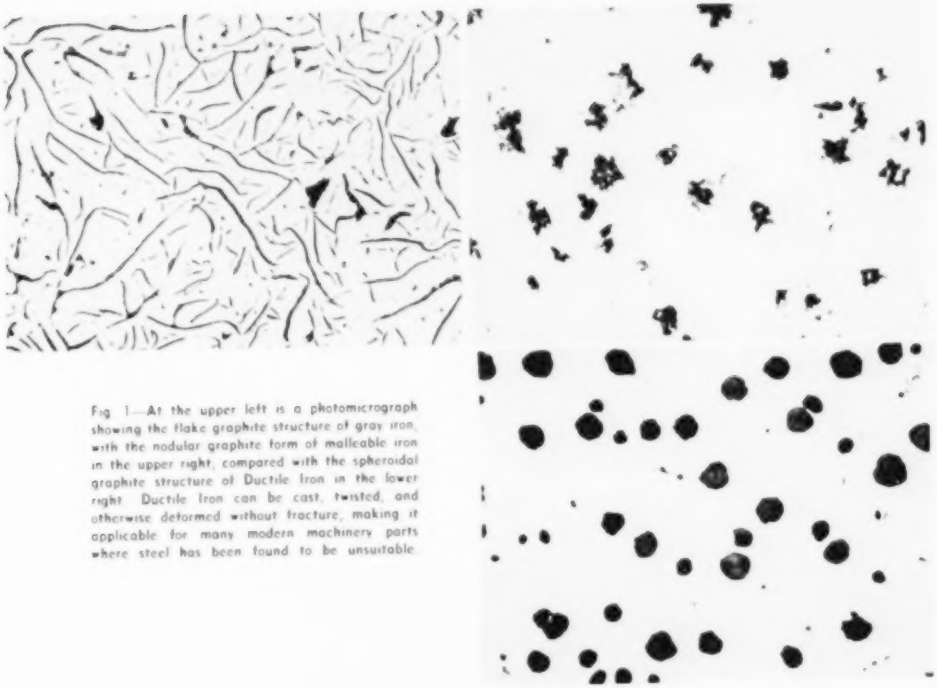

Fig. 1—At the upper left is a photomicrograph showing the flake graphite structure of gray iron, with the nodular graphite form of malleable iron in the upper right, compared with the spheroidal graphite structure of Ductile Iron in the lower right. Ductile Iron can be cast, twisted, and otherwise deformed without fracture, making it applicable for many modern machinery parts where steel has been found to be unsuitable.

Ductile Iron Combines Properties Of Cast Iron, Malleable Iron, Steel

DUCTILE Iron, one of the outstanding foundry developments since the introduction of malleable iron in this country, was developed at the Bayonne Research Laboratory of the International Nickel Co. Paul D. Merica, president of Inco, in discussing high strength pearlitic malleable iron in his AIME Howe Memorial Lecture in 1937 said:

"It must impress us all alike that invention of this sort, breaking through the bounds of our conventional conception of materials, may be expected to bring in its train other similar and equally useful developments and should, when practiced in the *no man's* land bordering cast iron, serve to extend still further the limits of usefulness of this maerial. Such developments tempt us to hope that we may sometime even attain that ideal objective—ductile gray iron!"

In Ductile Iron, the graphite is in the form of spheroids, as distinguished from the flake graphite of gray cast iron, and the nodular or irregularly round graphite forms found in malleable iron, as shown in Fig. 1. Ductile Iron can be bent, twisted, and otherwise deformed without fracture, and has several times the strength of ordinary gray iron. Its outstanding strength as well as ductility, in addition to exceptional resistance to shock, is especially useful throughout the industrial world. Modern machinery has many parts which are too intricate to be cast in steel, and which have inadequate mechanical properties when cast in gray iron.

Spheroidal graphite iron produced with cerium was announced in 1948, at about the same time T. H. Wickenden and L. B. Pfeil developed a means of producing spheroidal graphite iron using magnesium at Inco. In 1949, 3500 melt tons of Ductile Iron were produced in the United States and Canada. This was increased to 20,000 tons in 1950, over 50,000 tons in 1951, and is expected to reach 80,000 to 100,000 tons in 1952. Over 200 companies operating 500 to 600 foundries in all parts of the world are producing Ductile Iron under license, with castings ranging from a few ounces with sections as light as

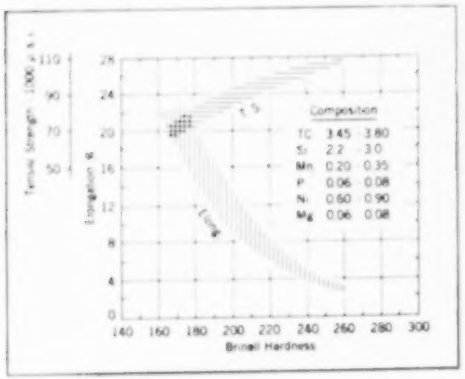

Fig. 2—The graph shows the relation between tensile strength, elongation and hardness of Ductile Iron. It reflects the proportion of pearlite and ferrite in the microstructure. A hardness measurement on a particular casting indicates the strength and ductility of the casting.

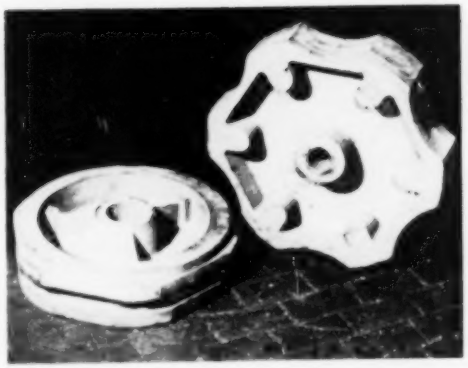

Fig. 3—Fixture castings for jet aircraft are among the many applications for Ductile Iron, whose particular properties have found application in a variety of machines. Because of its high fluidity, it can be used to fill intricate molds. It also has excellent mechanical wear resistance.

1/10 in. thick, to 50-ton anvil blocks having sections 48 in. thick.

Properties representative of the bulk of the production of Ductile Iron are given in Table I. The two as-cast grades differ in that the first is substantially pearlitic and has maximum strength, while the other, with its lower manganese and nickel content, has a ferritic-pearlitic structure, resulting in lower strength and increased ductility. Annealing of either of the first two grades for a few hours produces fully ferritic structures generally having about 70,000 psi tensile strength and 20 pct elongation.

Table I. Representative Mechanical Properties of Commercial Heats of Ductile Iron

Condition	Strength, 1000 Psi		Elong., Pct	Bhn
	Tensile	Yield		
As-cast	80 to 100	70 to 75	2.5 to 3.5	225 to 265
As-cast	65 to 80	65 to 70	5.5 to 10	190 to 225
Annealed	65 to 75	50 to 60	17 to 23	140 to 180
As-cast	85 to 90	80 to 75	1.0 to 3.0	230 to 290

tion. There are a number of basic lined cupolas in operation from which elongations of 10 to 15 pct are obtained in the as-cast condition. The fourth grade shown is higher in phosphorous, and thus not as tough as those preceding.

In Ductile Iron, there is a relationship between strength, hardness, and elongation, as shown in Fig. 2, which reflects the proportion of pearlite and ferrite in the microstructure. Thus, a hardness measurement on a particular casting, providing other conditions are met, will indicate the strength and ductility of the casting. This relationship applies to Ductile Iron that is free of primary carbide, that contains less than 0.1 pct phosphorous, and is fully sound. Properties of heat treated Ductile Iron are given in Table II.

The broad compositional range is shown in Table III. The carbon content of Ductile Iron is higher than in gray iron. The carbon equivalent, carbon + 1/3 silicon, is generally about 4.3 pct. It varies from below 4.3 pct for medium and heavy sections, to 4.6 pct for light sections utilizing hypereutectic irons.

Fig. 4—This Ductile Iron spout of a pouring trough carried 27 million lb of molten aluminum at temperatures up to 1400 F in 18 months.

Fig. 5—A gray iron spout, working under the same heat and load conditions, cracked in three months and had to be replaced.

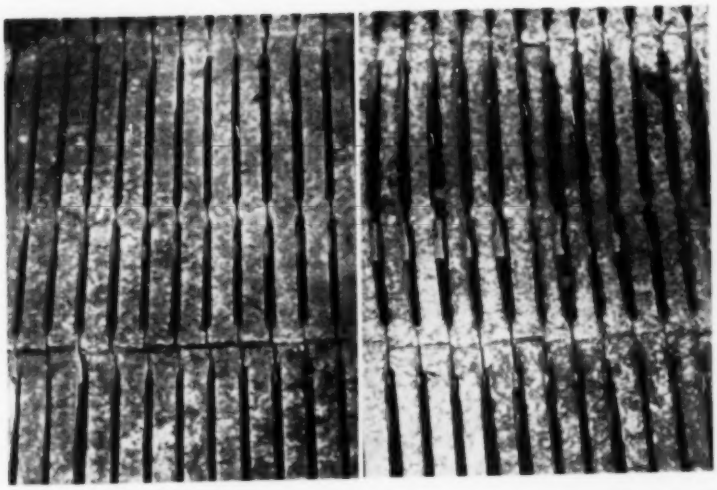

Fig. 6—The Ductile Iron grate on the left and the gray iron grate on the right were used on a sintering furnace for one month. Performance for the Ductile Iron grate was superior.

Magnesium, used in the ladle to control the graphite form, has little effect on the properties of the matrix. These matrix properties are controlled by silicon, manganese, nickel, molybdenum, chromium or other carbide forming elements, the cooling rate of the casting in the mold and the phosphorous level. Although phosphorous does not interfere with the formation of spheroidal graphite, it lowers the properties of Ductile Iron, particularly elongation and toughness. Silicon has no marked influence on the shape or distribution of the spheroids in Ductile Iron, and is an important alloying element. Each addition percentage increases the strength approximately 11,000 psi.

Table II. Heat Treated Properties of Ductile Iron

Heat Treatment	Strength, Psi Tensile	Strength, Psi Yield	Elong. in 2 In., Pct
Normalized and Drawn			
Air cooled 1600°F	135,750	89,250	7.0
Air cooled 1600°F, Drawn 1100°F	137,000	93,000	7.0
Air cooled, 1600°F, Drawn 1200°F	138,000	95,000	8.0
Oil Quenched and Drawn			
Oil Quench 1550°F, Drawn 900°F	152,750	136,250	2.0
Oil Quench 1550°F, Drawn 1000°F	152,750	137,250	4.0
Oil Quench 1550°F, Drawn 1100°F	135,500	121,500	7.5
Oil Quench 1550°F, Drawn 1200°F	101,250	84,000	10.0

Nominal Composition, Pct: 3.50 Total C, 2.30 Si, 0.35 Mn, 0.05 P, 0.01 S, 1.25 Ni, 0.06 Mg.

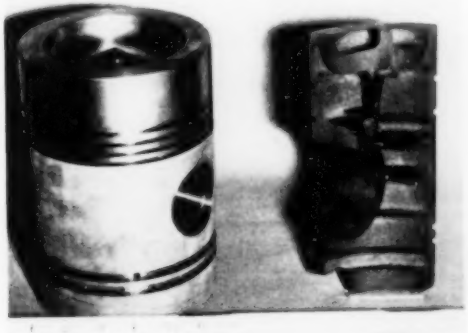

Fig. 7—Ductile Iron diesel pistons are being designed which will have the same weight as aluminum pistons. A large number of Ductile Iron pistons are now in use in diesel engines.

Table III. Composition Range of Ductile Iron, Pct

	Broad Range	Ferritic High-Ductility	Ferritic High-Strength	Pearlitic High-Strength
C	3.2 to 4.2	3.6 to 4.2	3.4 to 3.8	3.2 to 3.8
Si	1.0 to 4.0	1.25 to 2.0	2.25 to 3.25	2.25 to 2.75
Mn	0.1 to 0.8	0.35	0.35	0.6 to 0.8
P	0.10	0.08	0.10	0.10
Si	0.0 to 3.5	0.0 to 1.0	0.0 to 1.0	1.5 to 3.5
Mn	0.05 to 0.10	0.05 to 0.08	0.05 to 0.08	0.05 to 0.08

Ductile Iron has high fluidity, and can be used to fill intricate molds. The combination of high mechanical properties, good fluidity and castability should lead to its widespread use in pressure castings. In many applications it has successfully replaced steel, malleable iron, bronze, and gray iron at a substantial cost saving.

The material has excellent mechanical wear resistance, equalling that of gray iron. Its resistance to heat and oxidation at elevated temperatures is superior to gray iron. In fatigue resistance, Ductile Iron compares with ordinary grades of steel. It will also sustain the same shock loads as ordinary steel having the same yield strength. Ductile Iron can be arc welded with the same techniques established for gray iron. It is being used in several applications solely because of its weldability. The material also has good machinability.

Ductile Iron combines the process advantages of cast iron with the product advantages of steel. Because of its properties it can be used in many applications, replacing other materials. In addition, because it can be produced in a cupola, Ductile Iron has a high degree of flexibility with respect to size, intricacy, and number of castings that can be produced at any given time.

Open Hearth Zebra Roof Experience Analyzed

by T. H. Harley

AN extensive survey to determine the extent, type, and results of the use of Zebra roofs covered 63 open hearth shops in the United States and Canada. Replies were received from 47 shops, or 75 pct of the plants contacted, employing 635 furnaces. These 635 furnaces, tapping heats ranging from 30 to 450 tons, represent 65 pct of the open hearth furnaces in this country and Canada. Of the 47 plants reporting, all but four, with a total of 29 furnaces, had experimented with or used the Zebra roof. Results of the survey are given in Table I.

The question that can probably be considered of most importance was that regarding the future use of Zebra roofs. An effort was made to further analyze the extent and results of the Zebra roof in classifying its use by furnace heat sizes, as shown in Table II. There were seven furnaces in plants with 450 ton furnaces which claimed no benefit from Zebra roofs.

As far as the survey determining what might be termed a standard Zebra design, 90 pct of the plants reported using a ratio of one silica to one basic ring. Approximately 80 pct of the plants use alternate long and short lengths of basic brick rings. Eight plants reported using basic brick rings of the same length. Four of these plants reported favorable Zebra success, three unfavorable, and one questioned the use of Zebra construction.

Numerous Zebra roofs of the same design, reported employed successfully in some shops, were found unsuccessful in other shops.

Plants using basic brick keys were 22 in number, compared to 11 plants using wedges. Four plants used both keys and wedges. Of all plants reporting, 85 pct used unburned basic brick in roofs, compared to 15 pct using the burned variety. All plants reported using the plated type of basic refractory.

Among the comments received from plants that have not realized benefits from the use of the Zebra roof were:

The Zebra slows down the installation of the roof; the Zebra slows down hot patching because of difficulty in knocking out the basic brick; Zebra roofs are unstable and must be braced early in the campaign—they are very sensitive to mechanical abuse, and buckling frequently causes the loss of a roof that could ordinarily be patched; seven Zebra roofs averaged 30 heats less than 26 regular roofs in the same period. Zebra roofs were eliminated in two shops with as good or better roof life since elimination—the shop now using Zebra has no better roof life than prior to using Zebra, but has increased fuel consumption and experienced tonnage decreases from tap to tap, and does not believe that the Zebra has shown any benefit, but with certain practices Zebra has possibilities.

Shops reporting favorably on the use of Zebra roof stated:

Zebra roofs reduce hot patching; Zebra construction used only in vulnerable areas and not in the entire length of the roof; Zebra roof a valuable asset to operation (several plants); wedges preferred for faster installation time; while some reduction in hot patching time and increased campaign life has been achieved, not entirely convinced the practice is economically sound (several plants).

It appears from the basis of the results of the survey, the use of Zebra roofs has been successful on two out of every seven furnaces, unsuccessful on four out of every seven furnaces, and questionable on one out of seven furnaces. An analysis of replies received from all plants indicates that there are no definite trends showing where Zebra design will perform satisfactorily, or where it will be unsuccessful. The answer probably lies in the old practice of cutting and trying in each individual application.

Appreciation is expressed to all who cooperated in helping to make this survey possible.

Table I. Summary of Results Obtained in Survey on Use of Zebra Roof

Question and Answer	Plants, No.	Furnaces, No.	Furnaces, Pct
Total plants to whom survey was sent	83		
Total replies received	47	635	65
Zebra roof experience	43	606	60
No Zebra roof experience	4	29	5
Have the number of heats to the first roof patch increased with Zebra construction? (43 plants, 606 furnaces)			
Yes	20	279	46
No	17	250	41
No reply	6	77	13
Has roof life increased with use of Zebra roof? (43 plants, 606 furnaces)			
Yes	15	158	26
No	21	365	60
No reply	7	83	14
Has furnace campaign life increased with use of Zebra roofs? (43 plants, 606 furnaces)			
Yes	12	133	22
No	23	383	63
No reply	8	92	15
Has furnace availability increased with use of Zebra roofs? (43 plants, 606 furnaces)			
Yes	10	121	20
No	23	387	64
No reply	10	98	16
Has tonnage increased with the use of Zebra roofs? (43 plants, 606 furnaces)			
Yes	12	130	21
No	21	366	61
No reply	10	110	18
Has use of Zebra roofs reduced furnace masonry? (43 plants, 606 furnaces)			
Yes	6	63	10
No	27	439	73
No reply	8	104	17
What are your intentions regarding the future use of Zebra roofs? (47 plants, 635 furnaces)			
Will discontinue and watch future developments	21	340	54
Will continue use of Zebra roofs	15	153	26
Use questionable, or will continue experimentals and watch further developments	7	97	15
Never used Zebra roof	4	29	5

Table II. Future Use of Zebra Roofs Classified by Furnace Size

	Furnace Size, Tons							
	30 to 99		100 to 149		150 to 199		200 to 250	
	No.	Pct	No.	Pct	No.	Pct	No.	Pct
Will discontinue and watch future developments	25	58	117	55	109	64	97	52
Will continue use of Zebra roofs	7	17	64	30	34	22	58	31
Use questionable, or will continue and watch further developments	10	24	33	15	22	14	32	17
Total	42	100	214	100	156	100	187	100

T. H. HARLEY is a Ceramic Engineer in the Steel Div. of Ford Motor Co. This paper was presented at the National Open Hearth Steel Conference, Pittsburgh, Mar. 31, 1952.

Material Selection Factor Significant in Bourdon Tubes

by J. B. Giacobbe and A. M. Bounds

THE Bourdon tube is the actuating element for the majority of pressure and temperature indicating and recording instruments. In general the Bourdon tube, oval or elliptical in cross-section, and coiled in the form of a C, a spiral or helix, is sealed at one end and connected at the other end to a capillary or passage tube through which the pressure is transmitted. Under pressure the confined fluid, either gaseous or liquid, inside the tube tends to force the walls into a circular cross-section, causing the coiled tube to straighten out slightly. This produces a quasi-linear deflection at the sealed end of the tube which is known as *tip travel*. It is this tip travel that is then translated by means of mechanical (sector and pinion) or electrical linkage into registrations on the face of a dial or chart, recording either temperature or pressure. Some tubes are linked into an alarm system and must close a switch at a designated point in the tip travel. Still others must do heavier work in actuating recording mechanisms, (as in pressure and temperature recorders) as well as close or open control switches in pressure or temperature control mechanisms, or open and close valves mechanically.

Shaping of Bourdon Tubes

Some gage manufacturers produce their own Bourdon tubing from round, redraw stock. Most, however, obtain tubing in straight lengths preshaped to an intermediate oval or elliptical cross-section which can be formed or coiled directly into the required Bourdon tube specification. Starting with a pre-shaped tube as supplied by the specialty redraw mill, mandrel and sand-fill coiling are two of the most common forming methods.

Mandrel coiling involves at least two basic steps. Tubing into which has been placed an internal mandrel, is flattened by being pulled through forming rolls, so adjusted as to bring the major axis of the Bourdon tube to within the required limits. Coiling then is accomplished by clamping one end of the tube to a circular forming roll and rotating the roll as pressure is exerted by a second forming roll against the outside of the tubing. A mandrel also is used in this operation, its tip projecting to a point near that at which the tube starts to bend. Coiled Bourdon tubes are then cut off from straight sections individually.

Sand-fill coiling is a slower process and not as well adapted to mass production as the mandrel-coiling method. When tubing is ready to be coiled, short lengths slightly longer than the desired finished length are cut and one end tightly closed, usually by crimping and soldering. The tube is then filled with a fine sand, wood's metal or rosin, or some other fine granular material. The remaining tube end is then sealed. In this method the filler serves as a mandrel, preventing collapse as pressure is exerted inside the tube. After coiling, tubes are unclamped, the crimped ends sawed off, and the filler material removed.

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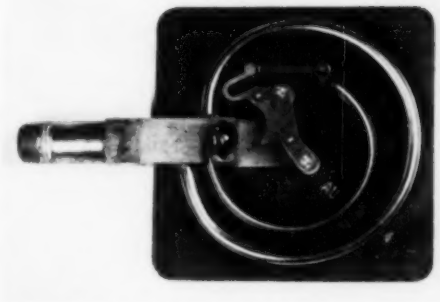

The working parts of a conventional type of pressure gage are shown. The Bourdon element (inner tube) is coiled about 260° and is roughly half round in cross-section.

Classification of Alloys by Temper

The large number of alloys used for Bourdon purposes can be classified into groups on the basis of the treatment necessary to obtain the *temper* or hardness level required for a specific application. Such a grouping may be made as follows:

Group I—Strain Hardened; cartridge brass, Trumpet brass, phosphor bronze, silicon bronze, austenitic stainless steel (AISI Types 304 and 316), monel.

Group II—Precipitation Hardened; beryllium copper, K Monel, Ni-Span C, Inconel X.

Group III—Heat Treated (Quenched and Drawn); low alloy steels (AISI 4130, 8630), martensitic stainless steel (AISI Type 403).

Although this grouping shows the common alloys used for Bourdon tube application, it is by no means exclusive since many other alloys used for the same application would fall into one or the other of the above groups.

Characteristics

The alloys in Group I are supplied in the strain hardened (cold worked) condition for Bourdon tube purposes. Either a certain hardness range or a given amount of cold reduction is specified by the gage manufacturer. In addition, close grain size control is maintained in order that uniform performance from one Bourdon tube to the next can be expected.

These materials are apt to show some drift, hysteresis, and relaxation (cold creep, zero shift) and are not generally used in high-precision gages, but are widely used in low pressure gage applications. Ordinarily, this group does not require heat treatment after coiling although stress relieving at low temperatures can be used to advantage in improv-

The most common type of Bourdon tube is the circular segment shown at the left. Others are the spiral coil (center) and helical coil (right). The spiral and helical coil are not usually found on indicative gages where power sufficient to move a needle pointer is all that is needed.

ing the precision of the gages. The copper alloys in this group are relatively easy to form (coil).

Group II alloys as preshaped in random or cut length tubes are generally supplied either in the slightly strain hardened (approximately ¼ hard) condition or to a specified hardness range, but after forming this group must be precipitation hardened to obtain optimum operating characteristics. These alloys are likely to develop some distortion during heat treatment because of specific volume changes which occur in the metal during precipitation. Therefore, jigging or clamping usually is necessary. On the other hand Group II alloys produce high precision Bourdon tubes possessing good creep resistance, low hysteresis and low relaxation. These alloys are more difficult to form than the alloys of Group I and should be obtained from the tube mill in the softest possible condition. Fatigue life of alloys in this group is usually excellent, although under conditions of corrosion, early failure may result.

Group III alloys are generally supplied in soft annealed condition; however, for extremely light wall tubing it is desirable to obtain tubing *as shaped*, in order that specified dimensional tolerances can be maintained.

Alloys in Group III are not difficult to form, being intermediate between Groups I and II in workability. The martensitic stainless steels (Types 403 and 420) are somewhat more difficult to form than the low alloy tubing (4130, etc.) because of higher base hardness or strength. These alloys must be quenched and drawn (tempered) after forming to obtain the necessary mechanical properties. They can be used in high pressure applications and show exceptionally good characteristics with respect to creep, hysteresis, and zero shift. Endurance limits of these alloys are also high, provided the surface of the original tubing is free of imperfections such as seams, gouges, etc. Particular precautions as to surface quality must be taken with the low alloy steels of Group III because of certain defects invariably occurring during piercing and hot working of the seamless tube rounds.

Corrosion Resistance

Corrosion resistance for Group I alloys is good for ordinary atmospheric exposure. Copper base alloys are adversely affected by compounds containing sulphur, ammonia or mercury. In this group, the austenitic stainless steels show maximum corrosion resistance. Monel also shows good corrosion resistance to many chemicals.

Corrosion resistance of the alloys in Group II may be considered excellent. Beryllium copper compares favorably with deoxidized copper with respect to corrosion resistance. It is particularly resistant to corrosion by brine solutions, mine waters, paper mill sulphite, etc., but should not be used in contact with strong acids such as sulphuric and nitric acids. Although many of the copper base alloys are susceptible to stress corrosion cracking (season cracking), beryllium copper resists this phenomenon to a high degree in all tempers and hardness levels.

Where corrosion resistance is not a primary factor, low alloy steels provide a combination of excellent Bourdon qualities including accuracy in both high and low pressure work, good operating characteristics, and maximum economy. However, where a high degree of corrosion resistance, high mechanical properties and high modulus are indicated, the hardenable stainless steels of Group III are recommended.

Joining

Except for silicon-bronze and the austenitic stainless steels, the alloys of Group I are readily soft soldered and brazed. Because of corrosion considerations, the most popular method of joining austenitic stainless steel is by inert arc or atomic hydrogen welding. Except for a slight deterioration in properties at the heat affected zone of unstabilized grades such as AISI Type 304, the corrosion resistance of the weld metal is essentially the same as that of the parent metal.

For joining the alloys in Group II, *hard* or silver solders must be used judiciously. Beryllium copper, for example, must be silver soldered or brazed prior to precipitation hardening since the joining temperature is considerably in excess of the hardening temperature. The usual technique involves brazing followed by water quenching from the annealing temperature, combining joining and solution annealing in one operation. Subsequent exposure of the assembly to hardening temperatures will not affect the joint. If soft solders are used to join beryllium copper after hardening, it is important that the temperature does not exceed 700°F.

For Inconel X, K Monel and Ni-Span C, silver brazing may be done either before or after precipitation hardening. However, if brazed after age hardening, these alloys will show a slight local softening due to the required brazing temperature. Silver solders having a low flow point should be used to minimize this effect.

Soft soldering the high nickel alloys of this group is practical but rarely used. The technique is limited to applications where corrosion is not an important factor. Furthermore, alloys such as K Monel and Inconel X develop surface oxide films which must be thoroughly removed either mechanically or chemically before soldering. Special acid fluxes are recommended to cut this oxide during joining.

The patented nickel alloys of Group II can be welded readily by metallic arc or inert-gas-metal-arc process. In addition, K Monel can be joined by the oxy-acetylene process. It should be noted that after age hardening, the properties of welds in this group of nickel alloys are not quite as high as those of the parent metal.

Because of the frequent use of the alloys in Group III in high pressure applications, high temperature brazing, welding, and threading of mating parts are the methods most often used in joining. Soft soldering is unsatisfactory because of the low strength of the joint. Welding and particularly threading of heavy wall tubes are most satisfactory from the standpoint of strength requirements.

Electrolytic Zinc Plant at Monsanto, Illinois

by T. I. Moore and L. A. Painter

THE electrolytic zinc plant of the American Zinc Co. of Illinois was described by Davidson[1] in 1944. Since then, improvements as well as expansion of the plant facilities have been made. In order to increase the production of high grade zinc which was needed for war purposes, an expansion program designed to double the slab zinc capacity was started in 1942 and completed in March 1943. This expansion was propagated by a contract between the American Zinc Co. of Ill. and the Defense Plant Corp. The contract included the facilities of the Fairmont City, Ill., property of the American Zinc Co., where a suspension-type roaster with contact acid plant, cadmium distillation furnace, Waelz oxide and densifying plant, and horizontal retort furnaces were installed.

The expanded Monsanto, Ill., plant and the additional facilities of the Fairmont plant were designed to integrate the metallurgical treatment of zinc concentrates for the production of special high grade zinc at Monsanto with the production of acid, cadmium, high grade zinc from furnace skimmings and the Waelz treatment of leach residue at Fairmont. In general, the original flowsheet was not changed, except for the addition of the filtering, drying and reclaiming of leach residue, and the treatment of purification cake for the recovery of copper, cadmium sponge, and zinc. Fig. 1 is a flow diagram of present operations. The original plant facilities, designed for 50 tons daily production of slab zinc, had some units which were more than adequate. Therefore, in expanding the facilities to 100 tons per day, it was not necessary to double all operating components. Table I gives the comparison of the changes made in the unit operating components for the original facilities, 1941, the 1943 expansion, and the 1951 facilities.

During the past 11 years a number of improvements have been made resulting in: 1—an increase in slab production, 2—higher recoveries on the calcine treated, 3—better quality of slab zinc produced, 4—higher current efficiencies, and 5—less man hours per ton of metal produced. In the summer of 1944, the "reverse" leaching process was placed in operation and since it has been described,[2] no further description will be given. Other facilities and changes which have contributed to the process improvements were the scrubbing of fume from the melting and

Table I. Changes in Operating Facilities

Operating Unit	1941	1943	1951
Calcine unloading (pneumatic), 10 tons per hr	1	2	
Calcine unloading track hpr. and elev., 60 tons per hr			1
Calcine storage, tons	1,000	2,000	2,000
Leach tanks, 35 vol. tons, No.	3	3	6
Slurry making 6x6 ft. stainless tank, No.			1
Ball mill, 4.5 ft x 16 in. conical, No.			1
Classifier duplex, No.	1		2
Thickeners, 50 ft diam, No.	2	3	370
Filter thickeners, sq ft	5,760	11,520	
Moore filters, sq ft		3	3
Drum filters, 10 ft diam x 16 ft, No.		1	2
Rotary dryers, No.			
1st stage Cu-Az purification tank, 90 vol. tons, No.			3
Solution heaters, No.			3
Filter press, 30x30 bronze, No.			4
Zinc dust purification tanks, 45 vol tons, No.	3	5	4
Filter press, 36x36 bronze, No.	3	5	3
Cadmium recovery plant:			
Process tank, No.		5	2
Cake roaster, 20 ft diam x 4 hearth, No.		1	
Filter press, 24x24, No.		4	1
Sponge wash box, 4x6 ft, No.			1
Evaporative cooling unit (vacuum), No.			1
Purified storage tank, vol. tons	400	400	400
Cell acid storage, vol. tons	400	400	400
Electrolytic cells, No.	180	372	372
Cell room ventilation, cu ft per min	45,000	125,000	125,000
Cell cooling water, gal per min	1,500	2,300	2,300
Deep well 16 in. x 95 ft, 1500 gal per min, No.	2	3	3
Melting and casting furnace, 130 ton, No.	1	1	1
Furnace fume scrubber unit, No.			1
Dross drums, No.			2
Dross roaster, 8 ft diam x 8 hearth, No.			1
Electrolysis power conversion, kw	6,250	23,750	23,750
Power transformers, 13,800/440, kva	1,000	1,500	2,000
Steam boilers fire tube, 15 psi, lb per hr	12,000	18,000	18,000
Steam boilers water tube, 125 psi, lb per hr			30,000
Air compressor, 2 stage, 300 cu ft per min, 100 psi, No.	1	2	2
Air compressor, 1 stage, 300 cu ft per min, 20 psi, No.			1
Vacuum pumps, 18x7, 720 cu ft per day, No.	2	3	3
Vacuum pumps, 24x11, 1,633 cu ft per day, No.		3	3
Building area, sq ft	60,854	113,568	115,000

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Discussion on this paper, TP 3373D, may be sent, 2 copies, to AIME by Jan. 1, 1953. Manuscript, March 26, 1952. New York Meeting, February 1952.

1. P. Davidson: New Electrolytic Zinc Plant of the American Zinc Company of Illinois. Trans. AIME (1944) 159, pp. 189-193.

2. L. P. Davidson, R. K. Carpenter, and H. J. Tschirner: Reverse Leaching of Zinc Calcine. Trans. AIME (1951) 191, p. 134; Journal of Metals (February 1951).

The Transactions papers appearing in the Journal of Metals during 1952 will subsequently appear in AIME Transactions, Volume 194, and may be permanently referenced to that volume.

Fig. 1 (above)—Plant flow diagram.

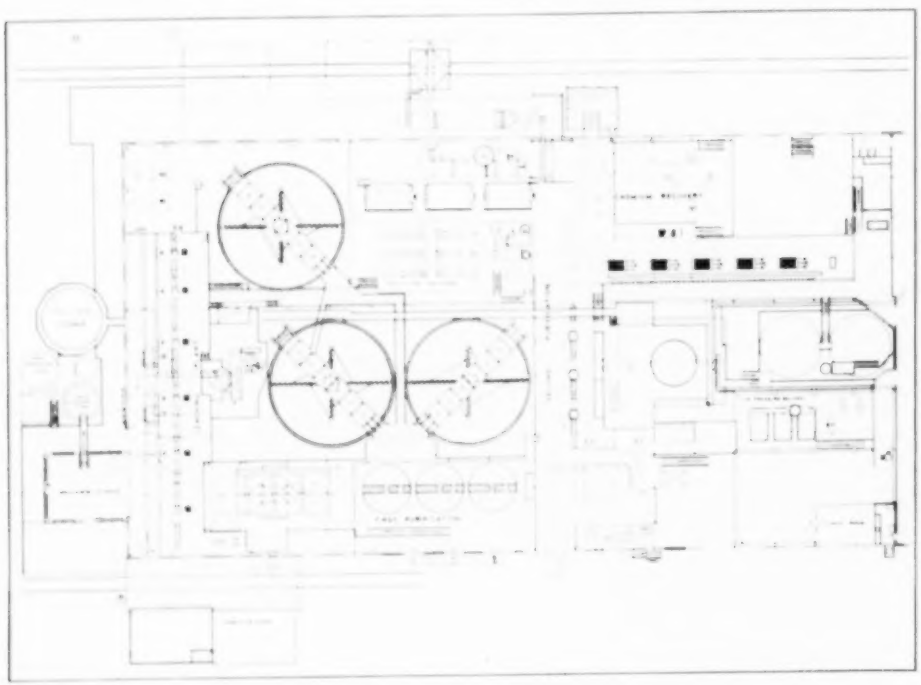
Fig. 2 (below)—Plan view of leach plant.

casting furnace, installation of two-stage Cu-As purification together with the required changes in clarification of raw leach solution and vacuum evaporative cooling, furnace dross treating plant, higher capacity for equipment handling the calcine material, unattended and automatic substation operation, and cell acid control.

Leaching

The leaching equipment and procedure in use at the present time have been described.[5] Fig. 2 is a diagram of the leach plant. Briefly, the leaching operation consists of the addition of spent electrolyte, about 130 g H_2SO_4 per liter, to a basic slurry prepared from spent electrolyte and calcine. The slurry, averaging about 1.45 sp gr, is prepared in a slurry mixing tank, Fig. 3, coupled with a classifier and ball mill. The main leaching operation is carried out in six lead and acid-proof-brick-lined tanks of 35 vol. ton capacity (a volume ton is equivalent to 240 gal). Maintaining the leach in a basic condition through most of the leaching cycle eliminates the settling and filtration difficulties encountered when calcines high in soluble silicates are leached in an acid condition. With good operating conditions, the leaching recovery of zinc other than that contained in zinc ferrite is comparable to the zinc recovery obtained with the original leaching system which consisted of adding calcine to spent electrolyte. The average analysis of the leach solution is as follows: zinc, 125 g per liter; copper, 0.25 g per liter; cadmium, 0.40 g per liter; arsenic, trace; iron, 0.01 g per liter; cobalt, 0.005 g per liter; and solids 29.0 g per liter. Usually 60 pct of the cadmium and 40 pct of the copper contained in the calcine is leached out.

Prior to the installation of the Cu-As purification step, the purifying effect of ferric hydroxide was of



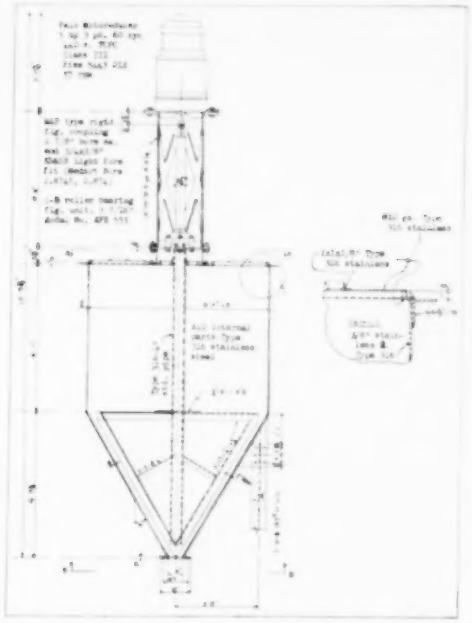


Fig. 3—Slurry mixing tank.

major importance in the production of solutions capable of electrolysis at reasonable current efficiencies. Ferric sulphate solution was made by dissolving scrap iron with spent electrolyte in eight lead-lined concrete cells of 3 vol. ton capacity and oxidizing the resulting ferrous sulphate with manganese dioxide (as manganese ore) in a wood stave, lead-lined tank. The capacity of this installation was insufficient to maintain the 0.6 to 1.2 g per liter iron addition which was considered necessary. In 1949, two 70 vol. ton brick and rubber-lined steel tanks were installed for the dissolving and oxidizing operations. Anode scale provided the bulk of the MnO_2 required for the oxidation reaction. Accurate metering of iron solution to the leach was provided by a rotameter in the iron solution line.

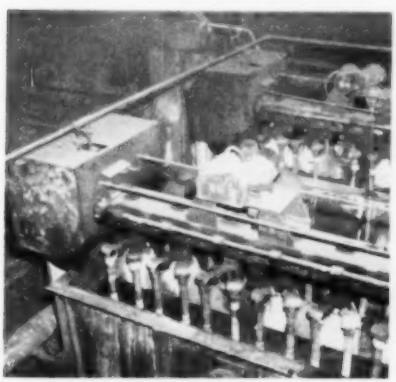


Fig. 4—Edco filter.

Since the addition of the Cu-As purification to the flowsheet, the use of the ferric hydroxide precipitate as a purifying agent has declined in importance and its use is now considered essential only in the case of certain concentrates. Operating procedure has varied between the addition of iron solution as a precautionary measure and the intermittent use of iron solution, depending on the type of concentrates currently being treated.

Clarification and Residue Treatment

Prior to the installation of the additional purification step in 1951, clarification of the leach liquor was carried out in three 50 ft Dorr thickeners. Test-plant work indicated that the feed to the Cu-As purification step should not exceed 0.1 g per liter solids, which seemed impossible to attain consistently with the existing Dorr thickeners. Since there was no room in the leaching plant for more thickening capacity in the form of 50 ft Dorrs, three Equipment Development Co. vacuum filter thickeners were installed, see Fig. 4. These units occupy only a fraction of the area of the Dorr thickeners employed. The filtering elements shown in Fig. 5 (24 to the unit) consist of stainless steel tubes, with suitable surface drainage, covered with specially woven nylon filter cloth. The filtering area per tube is 6 sq ft and the total filtration area for the three units is 369 sq ft. The tubes are suspended in stainless steel tanks into which the leach discharge pulp is pumped. The filtration cycle (filtration, flush back, and oscillation) is very short (35 sec) in

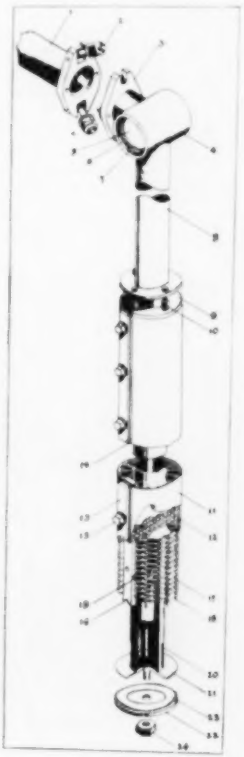


Fig. 5—Edco tubular filtering element.

1—Drain line connection
2—Disconnect swing bolt
3—Disconnect flange
4—Sight glass elbow body
5—Sight glass
6—Retainer gaskets and washers
7—Retainer ring
8—Main tube
9—Top cloth seal plate
10—Seal plate bolts and nuts
11—Filter medium cloth
12—Padding cloth
13—Vertical cloth seal strip
14—Vertical cloth seal gasket
15—Vertical cloth seal bolts
16—Vertical cloth seal bar
17—Supporting drainage spiral wire belt
18—Drainage spiral wire coils rods
19—Drainage belt attachment cotter pins
20—Filtrate entrance slots
21—Bottom closure plate
22—Bottom cloth seal plate
23—Bottom cloth seal gasket
24—Bottom cloth seal plate nut

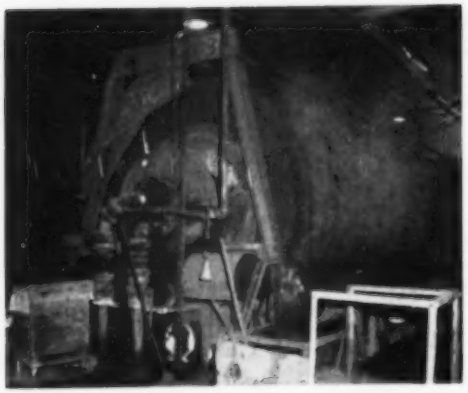


Fig. 6—Eimco filter.

order to take full advantage of the high initial filtration rate. Feed to the units averages 30 g per liter solids; the filtrate, 0.1 g per liter solids; and the underflow, 500 g per liter solids. The units, under proper operating conditions, are capable of filtering 270 gal per min; however, under long term operating conditions, the average filtration rate has been closer to 200 gal per min. The chief operating difficulty has been cloth blinding due to gypsum, to basic zinc salts, and to ferric hydroxide. More units have been ordered to make up for the deficiency in filtration rate but as a temporary measure one of the Dorr thickeners has been used in conjunction with the units of the Equipment Development Co.

Filtrate from the Edco filter thickeners and overflow from the above-mentioned Dorr thickener go to another Dorr thickener in service as a surge tank ahead of purification.

The third Dorr thickener is used as a residue washing thickener ahead of the rotary drum filters. The underflow from the filter thickeners is pumped into the washing thickener by air-actuated diaphragm pumps. Filtrate from the rotary drum filters, floor wash, and make-up water are also pumped into this thickener. The underflow from this washing thickener is pumped to three 10x16 ft Eimco rotary vacuum filter drums, Fig. 6. Originally all of these drums were of wood with steel internal braces, however, two have been replaced with drums of stainless steel construction. The drums are covered with nylon filter cloth over nylon backing cloth and are wire wound only at the ends of the drum. No scraper blades are used; a steam blow is sufficient to dislodge the cake which falls onto a belt conveyor leading to the driers. The filter cake, about 45 pct moisture, is charged by screw conveyors into two direct-fired rotary driers, one of which is a 6x50 ft Louisville drier and the other a 6x35 ft Ruggles Cole drier. Drier discharge, about 2 pct moisture, is carried by bucket elevator to a 50-ton capacity residue storage bin from which it is dropped into hopper cars and shipped out, usually to the Fairmont City plant. The analysis of dried residue is as follows: zinc, 28.9 pct; lead, 2.5 pct; copper, 0.99 pct; cadmium, 0.42 pct; and silver, 16.33 oz per ton.

Fig. 7—Heat exchanger open for cleaning.

Purification

The purification process until 1951 consisted of the addition of zinc dust, copper sulphate, and potassium antimony tartrate to the clarified leach discharge liquor in order to remove the cadmium, copper, and cobalt. This procedure was adequate to deal with calcines whose solutions contained under 5 or 6 mg of cobalt; however, when calcines yielding greater concentrations of cobalt were treated, a serious reduction in current efficiency resulted. The cobalt content of the calcine therefore imposed limitations on the choice of concentrates for the Monsanto plant and made necessary a search for a more effective purification. The Cu-As purification involving the use of arsenic trioxide, zinc dust, and copper sulphate was chosen. Test-plant work with this purification system indicated that not only cobalt but also other undesirable trace impurities were removed. The number of available zinc concentrates which could be successfully treated at the Monsanto plant was greatly increased. The tabulation of concentrates treated in 1950 and in 1951 shown in Table II is indicative both of the variety of the feed and the increase in the number of concentrates used.

About 27 pct of the feed during 1951 came from concentrates which could not have been successfully treated before the installation of the Cu-As purification. As a temperature of from 90° to 95°C was found to be the best for this purification, it was necessary to install heat exchangers, Fig. 7, to raise the temperature of the clarified leach liquors, which was about 65°C, to this temperature. Three helical-type heat exchangers utilizing 125 lb steam and capable of transferring 4,750,000 Btu per hr were installed for this purpose. Solution temperatures from the heat exchangers are recorded and controlled by Brown instruments. In actual operation, the average temperature of the solution in the purification tanks has been about 85°C and satisfactory purifications can be successfully made at this temperature.

The heated solution flows to any one of three 90 vol. ton wood-stave tanks, Fig. 8. These tanks are equipped with agitators constructed of 6 in. stainless steel pipe and driven by a 10 hp variable speed drive. Because of the formation of the very toxic gas, arsine, each tank is covered and vented by two stainless steel stacks: one a 12 in. stack with natural draft and the other a 24 in. stack with a 1.5 hp

blower whose discharge pipe extends into the pipe and is directed upward to assist the natural draft.

The procedure for the addition of reagents is as follows: The copper sulphate in crystal form and the arsenic trioxide in powder form is added near the beginning of the filling cycle. The usual additions are 250 lb of copper sulphate crystals and 4 lb of arsenic trioxide. When the tank is about two thirds full, about two thirds of the zinc dust is added and when the tank is completely full, the remainder of the zinc dust is added. The average addition is 400 lb of zinc dust.

As there is normally only about 4 hr available, including filling and discharging time, for each tank purification cycle, the tendency has been to standardize the reagent additions as much as possible. Most of the first stage purifications are made with the standard specified additions. Only occasionally is it necessary to add additional reagents. The solution in each tank is tested operationally for arsenic and for cobalt before it is discharged. The limits are 0.0001 g per liter of arsenic and 0.001 g per liter

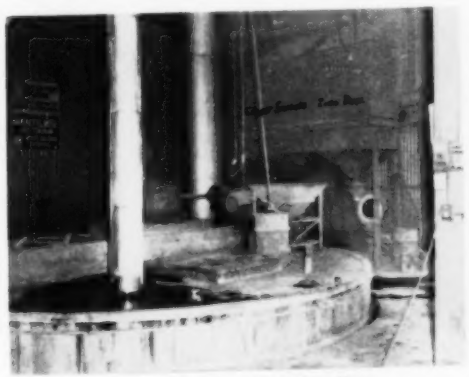


Fig. 8—First purification operating floor.

of cobalt. Before discharging, the solution is acidulated with spent electrolyte. Usually 15 pct of the cadmium in solution is precipitated in this step. An average solution analysis from this purification is 0.35 g per liter cadmium, a trace of copper, and 0.0001 g per liter arsenic.

The extreme toxicity of the arsine gas generated in this process has been a matter of grave concern. This department, although included in the main plant building, has been isolated from other departments by a wall which extends from basement to roof. The room used for storing the press cake from this process is also individually walled off and exhausted by two 12,000 cu ft per min blowers. As stated previously, the tanks are vented by blower assisted stacks capable of moving 1700 cu ft per min. Gas masks, available in case of emergency, are checked each shift. An escape chute leading to the outside is situated in the wall of the working level. Hand pump testers using silver nitrate paper are kept in a special locker. A tester consisting of a vacuum source, a rotameter, and a silver nitrate paper visible through a sight glass is in continuous operation. The tanks are scheduled for cleaning every two months and definite standardized procedures for entering tanks are used. A warning siren is turned on by the operator when the air in the room becomes contaminated or when the danger that it might become contaminated exists. The operators are given a urinalysis once every month and if the arsenic concentration is above the normal level, the operator's work habits are investigated and the operator is given another urinalysis. The attitude of the operators themselves is considered to be of major importance. No effort was made to minimize to them the potential danger of the process. In fact the danger was emphasized. The union committee and the whole plant personnel became acquainted with the danger and the necessary safety precautions through meetings and letters.

The solution from the first purification stage is pumped through four Shriver 30 in. bronze plate and frame presses equipped with individual hydraulic closers. The press cake is dropped through openings under the presses into the press cake storage room beneath. At three week intervals the stored press cake is loaded into trucks by a gasoline powered scoop truck and hauled to the Fairmont City plant.

The filtered solution from the first stage purification is treated with zinc dust in one of four 45 vol. ton wood-stave tanks for the removal of cadmium. These tanks are also covered and vented with 24 in. blower assisted stainless steel stacks. At the present time three of these tanks are agitated with stainless steel agitators made from 6 in. pipe, similar in design to those in use in the first purification stage, although they are driven at a constant speed of 38 rpm. As an experiment, one tank is equipped with a 30 in. propeller turning at 70 rpm in the center of a 44 in. diam x 6 ft long tube.

The zinc dust addition in this purification step averages about 175 lb per tank and is a more or less standard addition not subject to variation from tank to tank except on rare occasions. The solution is acidulated with spent electrolyte before discharging. The average tank purification cycle including filling and discharging takes about 3 hr. Tanks must be cleaned at least once a month because of the rapid accumulation of metallic zinc and cadmium sponge on the bottom of the tank.

The purified solution is filtered in four 36 in. Shriver bronze plate and frame presses. The average analysis of the purified solution is: 125 g per liter zinc, a trace of arsenic, and 0.0010 g per liter cadmium.

Because of the higher solution temperatures, the very troublesome gypsum condition encountered in

Table II. Concentrates Treated at the Monsanto Plant

Concentrate	1950 Tons	1950 Pct of Total	1951 Tons	1951 Pct of Total
Golden Manitou	17,436	24.9	18,503	27.0
Fresnillo	16,524	23.6	18,290	26.7
East Sullivan			5,346	7.8
Huanchaca			3,772	5.5
Missouri-Kansas			3,653	5.3
Wisconsin-Tri State			3,351	4.9
Atacocha	49	0.1	2,272	3.3
Tennessee Copper	4,664	6.7	2,012	2.9
Mascot-Universal	8,803	12.5	1,740	2.5
Calumet & Hecla			1,638	2.4
Potosi	3,842	5.5	1,397	2.0
Normetal			1,371	2.0
Buchans	8,806	12.6	1,312	1.9
Huaron	922	1.3	1,076	1.6
Volcan			858	1.2
Reocin	8,354	11.9	759	1.1
St. Joe Lead			685	1.0
Metalline			582	0.8
Cercapuquio	411	0.6		

Fig 9—Evaporating cooling diagram

the Shriver presses prior to the installation of the Cu-As purification step no longer exists. The solution temperature at the second purification stage in the Shriver presses averages about 75 C, which is excessively high for cell-room feed. Consequently, the solution is cooled from 75 C to about 33 C by a Croll-Reynolds two-stage, flash-type evaporator, Figs. 9 and 10. The flash tanks are made of mild steel and are each 3½ ft in diam and 10 ft long. Discarded electrolytic cell cooling water, which is about 18 C, is used again as cooling water for the evaporator condensers. Maximum flow of hot solution through the evaporators has been 340 gal per min with an entrainment loss of about 0.1 pct. An orifice-type flowmeter in the hot solution line records and controls the rate of flow into the evaporator and a weir-type flowmeter records the rate of flow from the evaporator discharge surge box. The original evaporator installation did not include any separators in the vapor pipes leading from the flash tanks to the condensers, consequently, severe solution losses were experienced and the maximum solution flow through the evaporators had to be kept at 240 gal per min. The installation of a centrifugal-type separator in the vapor pipe between the first stage evaporator and condenser enabled the whole unit to operate at a rate of flow somewhat in excess of the manufacturer's specifications and within the guaranteed solution loss figure. There is a rather rapid build up of gypsum in the evaporator flash tanks and their discharge lines. It has been necessary to clean these units once a week using both hot water recirculation and some manual cleaning.

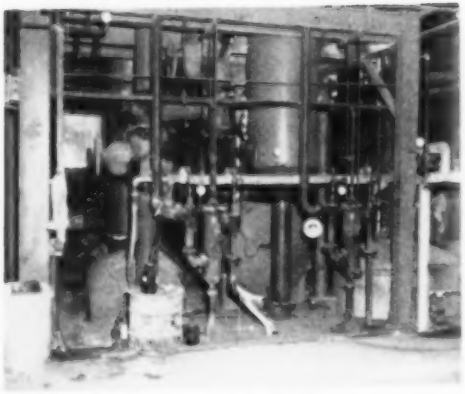


Fig 10—Evaporating cooling equipment

Cooled purified zinc sulphate solution is pumped to a constant head cone which supplies the cell room. Overflow from this cone flows to two 180 vol. ton wood-stave storage tanks. The average analysis of the purified solution is zinc, 135 g per liter; cadmium, 0.001 g per liter; arsenic, trace (0.0001); manganese, 1.3 g per liter; and cobalt, trace (0.001).

Cadmium Recovery

In conjunction with the plant enlargement in 1943, equipment was installed to recover the copper and cadmium as metallic sponges. This equipment consisted of a four-hearth, 20 ft diam Skinner roaster, an air swept hammer mill, five small wood-stave tanks, and five 24 in. Sperry presses. In brief, the process consisted of roasting the purification cake, leaching the roasted and pulverized cake in spent electrolyte, then selectively separating the copper and cadmium by accurate zinc dust additions. The cobalt was removed from the spent solutions by reaction with potassium ethyl xanthate before the solution was returned to the zinc circuit.

With the installation of the Cu-As purification with its complete removal of copper and cobalt, the treatment was reduced to merely that of cadmium recovery. The process now consists of the leaching (without prior roasting) of the Shriver press cake from the cadmium purification and the precipitation of the cadmium from the resulting solution.

The leaching operation is carried out in a lead and acid-proof-brick-lined, wood-stave tank equipped with the same type of agitator in use on the cadmium purification tanks. Due to the possibility of arsine generation, this tank is vented by a 24 in. stainless steel vent and blower of the same design as those in use on the Cu-As tanks. Purification cake including the Shriver press paper and tank cleanings from the cadmium purification tanks are added to a mixture of 60° Be sulphuric acid and water. Acid concentration is made as high as possible (usually 250 g per liter H_2SO_4) consistent with reasonable filtration rate of the resulting cadmium and zinc-bearing solution. Then the leach is pumped through a 24 in. Sperry bronze plate and frame press where the paper pulp and other insolubles are separated. The filtrate is treated with zinc dust in a 20 vol. ton lead and acid-proof-brick-lined, wood-stave tank agitated with a cone-type agitator. The cadmium concentration in the solution is only lowered to about 1.0 g per liter cadmium so that the production of a cadmium sponge low in zinc will be assured. The precipitated cadmium sponge is separated in a 5x9 ft steel box fitted with a stainless steel perforated plate. The spent cadmium solution is returned to the zinc circuit after passing through

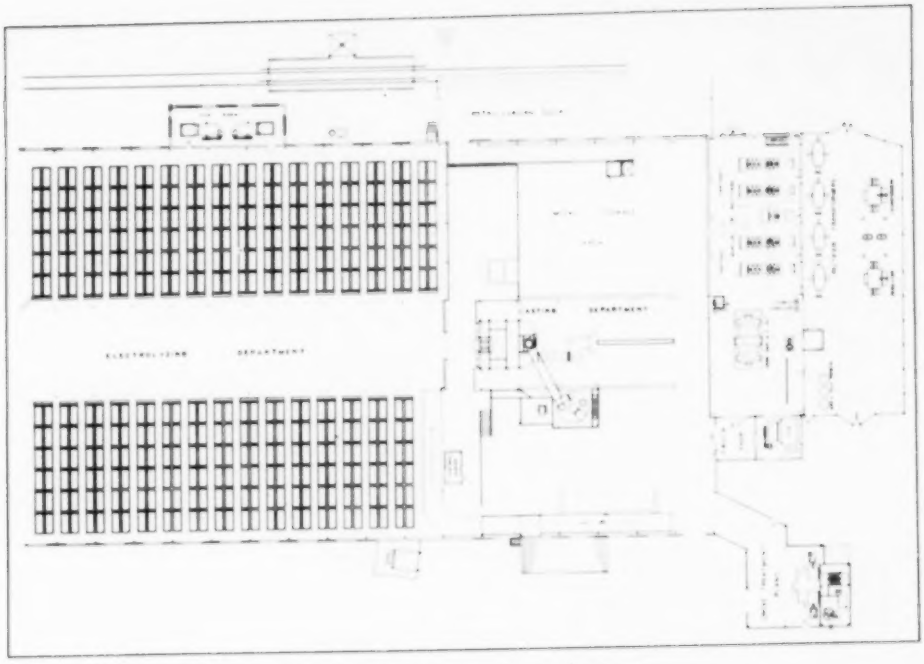


Fig. 11—Plan of electrolyzing and casting department.

a trap box designed to catch those particles of cadmium sponge not retained on the perforated plate. The cadmium sponge is washed with water until essentially all of the entrained zinc sulphate solution is removed. The sponge is then shoveled onto a 4x8 ft plate-type drier where the moisture content is lowered to a point where it is acceptable (about 20 pct) to the cadmium retort plant at Fairmont City. The average assay of the cadmium sponge is: cadmium, 82.0 pct; zinc, 2.0 pct; copper, 0.03 pct; and sulphur, 0.5 pct.

Electrolyzing Department

Two units of 180 and 192 cells in series comprise the electrolyzing circuits. Twelve cells arranged in two adjacent rows of six cascading cells are an operating unit or cascade with a 20 in. wide aisle as a working space between adjacent cascades. An area 44x300 ft between the two electrolyzing units adjacent to the lower cells of the cascades constitutes the stripping floor.

At the time of the 1943 plant expansion, reinforced proderite cell tanks were installed in lieu of the original concrete tank. The structural design of the proderite cell was found to be unsatisfactory. Within a year it was necessary to line the proderite tanks with 10 lb lead to make them hold electrolyte and later the proderite cells had to be replaced with lead-lined reinforced concrete cells. The present reinforced concrete cells have ½ in. reinforcing rods at about 6 in. centers welded at each cross of the reinforcing. The tanks are cast upside down. Each cell tank rests on six, lead-capped 5x5x3 solid glass blocks and is supported on reinforced concrete piers. The total load to be supported is 24,000 lb which consists of a concrete tank, 8000 lb; lead lining, 1300 lb; electrolyte 9900, lb; 27 aluminum cathodes with zinc, about 1000 lb; 28¼ in. rolled, punched 1 pct silver-lead anodes, 2800 lb; and copper bus bars, 1000 lb.

Current is conducted to and from each unit by copper cables equivalent to 33 sq in. of conductor. Anode and cathode electrodes rest on 2 in. wide bus bars mounted on the same side of the cell, supported on brackets fastened to the cell wall. Phenolic resin-impregnated laminated fiber glass insulating blocks are between the bars and brackets. In general, few changes have been made in the cells as originally designed except the proderite. Several types of cell linings are now under test in which plastic membranes and acid-proof brick are being tried.

The original 6 in. lead purified solution line feeding each unit has been replaced with a 6 in. Haveg line. Glue solution, when required, is pumped into the cell feed lines by a Lapp-Pulsafeeder so that a uniform distribution to each cell can be maintained.

Since 1951 the reagent strontium carbonate has been used for reducing the lead content of the metal produced. This reagent has been used in amounts varying from 4 to 12 lb per ton cathodes and in general has accounted for a reduction in lead content of the slab zinc produced of from 0.002 to 0.003 pct Pb. Because of its high specific gravity, it is difficult to keep the strontium carbonate suspended in a slurry unless high velocities are maintained. Hourly or continuous uniform feeding of the strontium reagent is desirable for good results. With high velocities, the abrasive characteristics of strontium carbonate as a slurry cause the circulating lines and pump to be destroyed, so that the first attempt to add the reagent hourly by squirting a measured amount into each cell from 30 positions on an iron

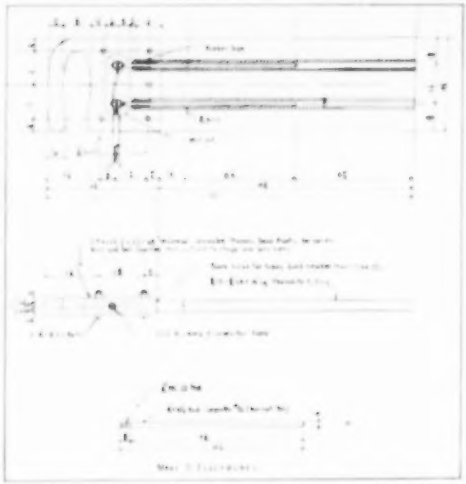


Fig. 12—Probe design

circulation line around the entire cell room failed. A measured amount of reagent is now added to the purified solution feed lines by splitting a circulating stream of reagent slurry.

Feed for all except the bottom cells of a cascade flows through a 1½ in. iron manifold 12 in. above the center of the cascade. A ¾ in. branch and valve is provided for each cell. The iron manifold is connected to nipples in the 6 in. Haveg line by a 2-in. hose. Since the installation of evaporative cooling, the rate of scale and gypsum deposit in these lines has increased. Wooden wine keg spigots are now being tried as valves for solution regulation of each individual cell feed.

Spent electrolyte is returned to cell acid storage sump by covered lead-lined wooden launders at the foot of the cascades.

In each cell 27 28 aluminum cathodes, which are 7/32 in. x 42 in. x 24 in., and 28 1 pct silver-lead grid anodes, slightly smaller than the cathodes, are in operation. Cathodes are positively spaced on 3 in. centers by indentations in glazed porcelain insulating blocks. Anodes are provided with three glazed porcelain cone separators, one at the center and one at each lower corner. Cathode edges are covered by general purpose synthetic rubber channels. These rubber channels have replaced the wood strip channels formerly used, and requirements are less than 1000 per month instead of the 2000 per day for wood channels.

Since 1947, aluminum cathodes have been fabricated and repaired in a shop designed for this work. Rolled and polished aluminum sheets together with lifting lugs are welded to a ⅝x2¾ in. extended aluminum header bar. A section of copper channel 3 in. long is welded to the bar for the electrical contact between the bus bar and header bar.

The present cathode design was evolved after experience with sheet and copper contact cast into header bars. Oxidation of copper and cast aluminum around the copper contact soon caused high resistance to the flowing current which resulted in poor deposition of zinc on the cathode. The cast bars were replaced by extruded bars welded to the sheets. The uniform size, greater mechanical strength, and corrosion resistance of the extruded bar have been most advantageous. One bar can be used for two new sheets before it is scrapped.

A change in contacts was necessary and ends of the extruded bars were first metallized with copper. Results with this were erratic. It was found that cadmium-plated copper could be readily welded to aluminum by an arc with standard aluminum welding rods. Adequate ventilation is provided where this welding is done to remove cadmium fumes. The welded contacts fail under severe mechanical shock but have been more successful and less expensive than any previous design.

Anodes are ¼ in. rolled and perforated 1 pct Ag-Pb alloy sheets. These are burned to chemical lead header bars cast around a copper bar. The lower edge of one end of the bar is exposed for bus bar contact. The sheet perforations are ⅜ in. sq and spaced on ⅞ in. centers.

Nine adjacent cathodes are lifted from the cells at one time by a ½-ton chain hoist hung on a strain insulator. Transport to the stripping floor is on an overhead monorail.

Two lead coils per cell, one at each end, cool the electrolyte. About 2200 gal per min of cooling water is pumped to the cell room from wells on the plant property.

Positive air pressure is maintained in the cell room to dissipate fumes by forcing in 125,000 cu ft per min of fresh air.

Cell Room Operation

Rated cathode zinc production is 128 tons daily. The average current is 11,800 amp. These meet ASTM special high grade zinc specifications.

Electrolysis is carried on at an average cathode current density of 36.5 amp per sq ft. The electrolyzing solution contains about 135 g per liter of zinc and is regulated to the upper ten cells of each cascade to maintain an acid concentration between 105 and 110 g per liter sulphuric acid. The tail cells are stripping cells and the spent electrolyte leaving them contains about 125 to 135 g per liter sulphuric acid. Manganese depletion in the cells is about 0.5 g per liter. Cell temperature is normally maintained below 40°C. Acid concentration in each cell is tested nine times daily by measuring the conductivity of the solution.

Conductivity comparison measurement of known titrated acid concentrations in the cell has been used at Monsanto since shortly after the plant was put into operation in 1941. Further development and refinement of the method of cell acid determination was made in 1949. The original method consisted of a complete recording of acid concentrations for all cells and the use of this recording to adjust the flow of neutral electrolyte feed to maintain the desired acid concentrations. It was recognized that if means could be found to inform the operator of the conductivity test probe, that the acidity was high, low or satisfactory, within a desired control range, simultaneous flow adjustments could be made at the time tests were made. Fig. 12 shows the design of the probe now in use. It was developed by using a high speed conductivity recorder with adjustable control contacts. Three audio devices actuated by the recorder contacts were first used but the noise level of the cell room during stripping operations prevented clear and understandable signals reaching the probe operator. Several groups of red, white,

and green signal lights, visible to the probe operator at all locations in the cell room, are now in operation. Upon adjustment of the contact to the desired control range, the probe operator is advised, upon inserting the probe in the cell, whether the cell tested is high, low or the desired acid concentration. A red light indicates high acid, a green light, low acid, and a white light, that the concentration is within the desired acid range. If adjustment of the flow is desired, the probe operator makes it at the same time the adjacent cell is tested. The results of this control method have been very satisfactory. It not only maintains more uniform acid concentration but also requires one less operator per shift.

Cathodes are removed for stripping once each day and returned to the same cell. Nine adjacent cathodes, one-third of the number in a cell, are removed at one time and transported to the foot of the cascade. Zinc deposits are stripped from the aluminum by inserting the edge of a floor chisel under one corner of the deposit. Normally, the entire sheet can then be pulled off. Very strong adherence has occurred at times although it is not clear what has attributed to the adherence since the solutions contain no fluorine. Some correlation between rapid lowering of cell temperatures and sticking has been noted. Cathodes last about 18 to 20 months and usually fail because of corrosion of the sheet above the solution line.

Cleaning the cells and anodes requires the time of 21 men five days a week. One cascade is cut out each day, the electrodes removed and electrolyte pumped out. Also on six cells only the electrodes are removed, making a total of 18 cells of anodes cleaned per day. Anodes are trucked to a cleaning area to be scraped and straightened. Cooling coils are scraped clean and the accumulated cell sludge is shoveled out to be returned to the concentrate roasters.

The present cleaning process is laborious. Plans are being made to mechanize this work so that more cleaning can be done with the same or less labor. Hand chain hoists for lifting anodes have been changed to compressed air operated hoists. Hydraulic cleaning is being studied to eliminate hard scraping of the anodes.

Power Conversion Equipment

The power for electrolysis and for auxiliaries throughout the plant is purchased from the Union Electric Co. There are two 8000 kva and one 7500 kva underground, three phase, 60 cycle, 13,800 v cables. Power for auxiliaries is transformed by three 1000 kva, single-phase and one 500 kva, three-phase, 13,800/400 v transformers.

Electrical conversion equipment for the electrolytic process includes four 12 anode, 5500 amp, 700 v water-cooled mercury-arc rectifiers and two 5000 amp, 600 v dc generators driven by an 8400 hp, 13,800 v synchronous motor, the latter unit being used primarily to replace the rectifiers when they are removed from the line for repairs. The station arrangement places the oil-insulated, self-cooled type transformers outdoors, with the outdoor 13,800 v switch gear. The rectifiers, regulating the heat exchangers and the metal-clad, oil circuit breaker are on the first floor of the station directly below the rectifiers to which they are connected. The rectifiers, anode breaker, cathode breakers disconnect switches, duplex control panels, individual control panels, and motor generator set are mounted on the second floor at about the same elevation as the transformer secondary connection. Bus connection to the individual rectifiers are made below the rectifier assembly. The neutral or negative connection from the interphase transformers is carried across the station directly below the rectifier assembly.

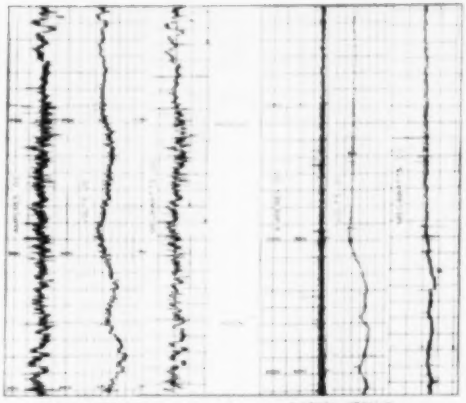


Fig. 13—Comparison of manual and automatic control for power rectifiers.

For normal operation, the four rectifier units are paired on both the alternating current and direct current sides of the station. There are two three-phase autotransformers, one with $7\frac{1}{2}°$ lead and the other $7\frac{1}{2}°$ lag, with the load ratio control feature, each connected to two 6-phase transformers making a 12-phase unit for a paired rectifier assembly and 24-phase for the entire station.

The operating advantage of the rectifier installation over the rotating apparatus installation is particularly emphasized by the problem of restarting the motor-generator unit after a power failure or shut-down. With rectifiers, all dc and ac breakers remain closed and the cell load is picked up by energizing the ignition circuits of all rectifiers simultaneously. The time element, in re-establishing service after power interruption, is very small for a rectifier as compared to a motor generator set. Other advantages are less maintenance, simplified cooling system, and higher overall efficiency of about 95 and 93 pct power factor. Because of the high operating reliability of the rectifier, arrangements were made to automatically control the cell load from the supervisory control center located just outside the cell room. This eliminated a station operator on each shift. Automatic current regulation, by means of a Leeds-Northrup Micromax ampere recorder, first actuates a motor-operated ignition control rheostat for a 4 pct voltage change and, if necessary, further changes are made by load ratio control transformers. Load characteristics of the cell room are sensitive to voltage changes. A 1 pct change in voltage makes about 5 pct change in current. This load characteristic makes it necessary to regulate frequently because changes in the incoming voltage from 12,500 to 14,500 are not uncommon. Fig. 13 compares the results obtained by automatic constant current control over the manually controlled rectifiers.

Current efficiencies for each cell room are determined by integrating the daily recorded ampere charts traced by two Leeds-Northrup recording po-

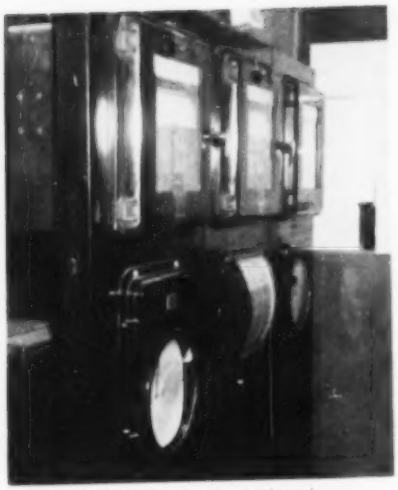


Fig. 14—Cell current control panel

tentiometers (Fig. 14) connected to their respective calibrated shunts in the cell circuits.

Cathode Melting

Weighed cathodes with an estimated 0.5 pct moisture are melted in a 130 ton suspended arch, natural gas fired, reverberatory furnace. Combustion is produced by three low pressure, Denver Fire Clay, natural gas burners equipped with manually operated fuel-air ratio regulators. A Leeds-Northrup Micromax recording pyrometer records metal bath and product of combustion temperatures. This instrument is equipped with high and low control contacts for both recorded phases of the operation. By means of a motor-operated gas valve, the firing rate is controlled according to the limit set for the stack and metal temperature. If the metal temperature is low, the gas is increased until the maximum metal stack temperature is reached at which point the gas firing is reduced. The results from the use of this automatic control were beneficial in the maintenance of a uniform melting condition in the furnace and produced a higher rate of conversion from cathodes to slabs.

Furnace draft is induced by the fume recovery unit and is automatically controlled to maintain about 0.05 in. of water at the burner inside the furnace at all times except during drossing and charging periods.

Casting Operation

There are two types of slabs produced at Monsanto: the familiar 60 lb slab and an interlocking slab of the same size. Until 1947, the overall slab dimensions were $18\frac{5}{8}$x$8\frac{3}{4}$x$1\frac{1}{2}$ in. and the slabs weighed 52 lb. In order to comply with the method of the Association of American Railroads for loading, bracing, and blocking carload shipments of zinc slabs, the overall dimensions of the slab were changed to $17\frac{1}{4}$x$8\frac{5}{8}$x$1\frac{5}{8}$ in. The slab weighed 60 lb. This change eliminated the need for longitudinal or center gate bracing, since the reduced slab dimensions would permit loading the car with six slabs the long dimension across the car for almost all box cars available at the Monsanto shipping point. The use of rast pallet slabs was also adopted at this time. A pallet load or unit load consisted of 32 regular slabs and four pallet slabs with an overall dimension of $34\frac{1}{2}$x$17\frac{1}{4}$x$21\frac{1}{2}$ in. high and weighed approximately one ton. This unit load proved to be very economical in loading as well as in reducing car bracing. Unit load or entire carloads are banded if necessary in order to meet the customer's specifications.

The entire casting operation is now being revised to incorporate a continuous casting machine. Since the finished design on this installation was not complete at the time this paper was written, no further reference to casting will be made here.

Slab zinc sample specimens are taken with a graphite ladle from the wells each hour during casting and make up the sample for spectrographic analysis.

Furnace Oxide Recovery

Zinc oxide in the furnace gases is recovered by water scrubbing, Fig. 15. This method is a radical departure from the more conventional cooling-trail and bag-house system for the recovery of oxide from zinc melting furnace gases. The unit was constructed after tests by the plant staff and is, as far as is known, the first instance of the use of water spray jets for this purpose. It offers the advantages of relatively low initial cost, low cost in maintenance and operation, simplicity, and small space requirements.

A 30 in. brick-lined flue connects the furnace to a vertical spray cooling tower of the recovery unit. A 24 and a 30 in. water jet fume scrubber are in series with the spray tower. These are mounted on the flat top of a 14 ft diam cone-bottomed steel tank. Two parallel baffles in the tank extend from the top into liquid in the body of the cone and divide the upper section into three chambers. The cooling tower is on the first chamber. A 24 in. duct leads from this to the 24 in. scrubber on the second chamber. A 30 in. duct connects this to the 30 in. scrubber

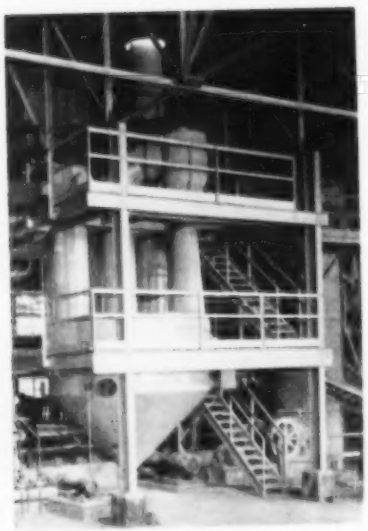


Fig. 15—Furnace fume scrubber

on the last chamber. Cleaned gas leaves the last chamber through a 30 in. steel stack.

The fluid passing through the cooling tower and scrubbers has two functions. It creates the draft necessary to draw furnace gases through the unit and by intimate contact and mixing, collects the contained solids.

Oxide washed from the flue gas collects in the lower part of the cone. The thickened pulp is withdrawn for 4 hr each day and fed to a 3x2 ft Oliver filter. The light pulp near the top of the cone is recirculated through the cooling tower and scrubbers by a 1000 gal per min centrifugal pump at 40 psi.

The oxide cake collected on the drum filter is washed with water to remove chlorine. The resultant zinc oxide filter cake is slurried with water and pumped to a spent electrolyte launder.

Furnace Dross Handling

During the last quarter of 1951, a new furnace dross handling system was put into operation. Prior to this time the melting furnace was drossed each day. Loose oxide was first raked into concrete buggies holding about 800 lb. These were dumped in a vented cooling room. Salammoniac was then worked into the metal bath and the remaining dross raked off after about 1½ hr. Large pieces of metal were pulled from the cooled dross the next day and returned to the furnace. A portion of the remaining metal was separated from the dross by a 4 mesh vibrating screen and returned to the furnace.

When the electrolytic plant was built, the melting furnace was adequate for the cathode production. All cathodes were melted and cast in five days. The amount of dross was small and the ratio of slabs to cathodes was high. In expanding the plant in 1943, the main objective was to provide as much high grade zinc as possible for war purposes. Assuming that the electrolyzing department was run at full capacity, additional production of high grade zinc could only be had by treating the skimmings alone. This was provided for by installing a gas re-

Table III. Data for Plant Operations, December 1951

Feed treated, tons	3,928
Zinc, pct	65.7
Lead, pct	1.0
Cadmium, pct	0.42
Iron, pct	0.2
Zinc dust used, tons	214.4
Based on cathodes, pct	6.0
Copper sulphate (25 pct Cu), tons	65.0
60° H_2SO_4 used, tons	433.0
Dried residue produced, tons	1,903
Zinc, pct	29.2
Lead, pct	2.6
Cadmium, pct	0.44
Copper, pct	0.92
Silver, oz per ton	10.94
Copper cake produced, tons	90.4
Zinc, pct	20.9
Cadmium, pct	4.24
Copper, pct	25.46
Cadmium sponge produced, tons	12.6
Cadmium, pct	77.74
Cathodes stripped, tons	3,553.5
Average amperes	10,710
Ampere efficiency, pct	89.49
Power consumption, kw-hr per lb cathodes, dc	1.581
Cathodes melted, tons	3,398.4
Slabs cast, tons	3,421.6
Ratio slabs to cathodes	0.951
Slab assay, pct	
Zinc (by difference)	99.9941
Cadmium	0.0024
Lead	0.0032
Iron	0.0003
NH$_4$Cl per ton slabs, lb	4.02
Skimmings produced, tons	59.0
Zinc, pct	82.5
Cathodes, pct	1.4
Labor, shifts per ton slabs	1.66

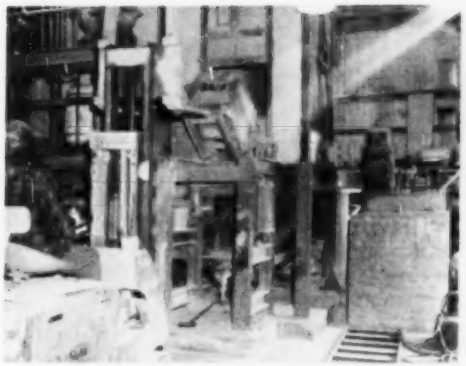


Fig. 16—Dross treating plant

tort furnace at Fairmont, Ill. With about 65 pct of the total zinc in the skimmings present as oxide, the shipping of a few more tons of metallic zinc to Fairmont did not justify additional equipment and labor to remove that small amount of metallic zinc at Monsanto. With the ever yearly increase in production of zinc at Monsanto, the continued practice of treating skimmings at Fairmont became uneconomical. Further, the handling of furnace dross was hard, hot physical work and the dust control was inadequate.

The introduction of dross drums and an eight hearth roaster with electric powered truck and other adequate handling equipment was made. These changes effected the following: 1—Dross drum treatment—Removal of molten metal from the skimmings for the return to the furnace. This cut the assay of the skimmings to 82 to 83 pct. 2—Roasting Skimmings—To remove chlorine and oxidized metallic zinc enabling the return of the roasted product to the leaching circuit. This gave about 3.5 pct more cathodes from the same tonnage of calcine fed. 3—Drossing on each shift.

Operation of Dross Handling Equipment

Raw dross is transported by electric fork truck from the furnace in skip containers which hold about 800 to 1000 lb. These skips are elevated by the electric truck onto an air operated tilting table which discharges the dross into the dross drums, as is shown in Fig. 16. The drum is rotated until it is ready to receive a second skip. A small amount of NH_4Cl is added to the charge to facilitate the separation of zinc from the dross. After several revolutions, the drum is stopped with the drain holes at the bottom and the molten zinc is allowed to drain into the launder. The molten zinc flows down the launder and is collected in a cast iron slag ladle. When no more molten zinc comes from the drum, the rotation is reversed and the dross discharges into a screw conveyor. From the screw conveyor it is elevated into a feed bin where it can be fed continuously into the dross roaster.

The dross roaster is gas fired to maintain a temperature of 800°C, which is sufficient to reduce the chlorine to 0.01 pct.

The data in Table III are those as of December 1951 and are indicative of the plant operation. Because of the "in process" inventories, tonnage figures for dried residue, copper cake, and cadmium sponge are not necessarily typical.

An Aid for Making Stereographic Plots When Working With Cubic Crystals

by Colleen Goldberg

IT is customary to plot crystallographic planes or axes on a Wulff stereographic net which is ruled with parallels of latitude and meridians of longitude. If a single crystal is placed at the center of a sphere, the coordinates of a crystallographic plane or axis are the coordinates of the point where the axis intersects the sphere. The standard (*HKL*) projection is the projection for which the sphere is rotated so that the (*HKL*) pole is at the center of the projection.

Schofield and Sachs and many others have published standard projections for the more important planes of a cubic crystal. With Tables I and II, it is possible to plot any plane (*HKL*) of a cubic crystal on a standard (001) projection if the absolute values of the individual *H*, *K*, and *L* are nine or less, which is almost always the case. Using the methods outlined by Barrett,[1] the standard (001) projection can be rotated so that any arbitrary plane is at the center of the projection.

The tables are believed to be important for two reasons: 1—The heretofore published standard projections usually are not of the proper size to fit the stereographic nets available. With these tables a standard projection can be made which will be of exactly the proper size for the available stereographic net. 2—With the tables, planes that do not appear on the previously published standard projections can be easily plotted.

For these reasons, the tables are especially useful in the study of optical reflections from etched surfaces and can also be used to make a standard projection for the axis which is normal to the macroscopic surface. (This axis can be found by X-ray or optical methods.) Then if the crystal is etched, the effect of the etchant can readily be determined by comparing the latitude and longitude of the reflecting planes (as determined with an optical goniometer) with the standard projection that has been prepared.

Use of the Tables

Fig. 1 shows the meridians and parallel which have been designated as zero longitude and latitude. The tables themselves are self-explanatory. The

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Discussion on this paper, TP 3328E, may be sent, 2 copies, to AIME by Jan. 1, 1953. Manuscript, Feb. 4, 1952.

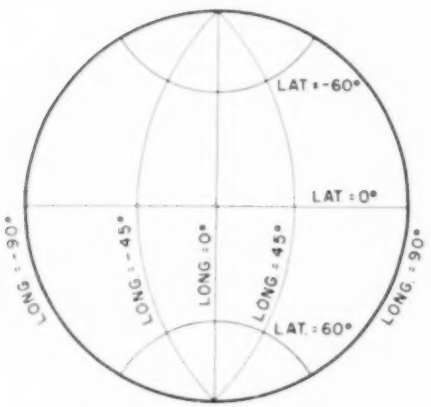

Fig. 1—Outlines of a Wulff stereographic net.

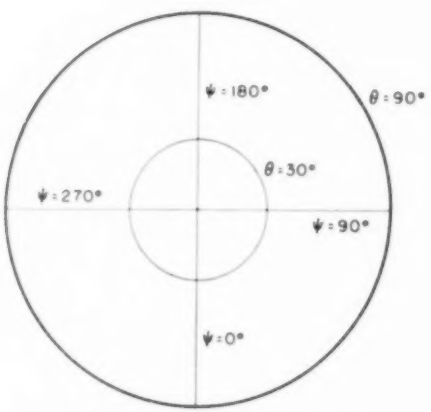

Fig. 2—Outlines of a polar stereographic net.

Table I. Longitude of Plane (*HKL*)

Longitude is positive when K is positive and negative when K is negative.
Longitude = 0° for all planes that have $K = 0$.
Longitude (*HKL*) = 180° − Longitude (*HKL*)

L \ K	1	2	3	4	5	6	7	8	9
0	90°00′	90°00′	90°00′	90°00′	90°00′	90°00′	90°00′	90°00′	90°00′
1	45 00	63 26	71 34	75 58	78 41	80 32	81 52	82 55	83 39
2	26 34	45 00	56 19	63 26	68 12	71 34	74 03	75 58	77 28
3	18 26	33 41	45 00	52 08	57 32	61 56	65 28	68 12	70 32
4	14 02	26 34	36 52	45 00	51 20	56 19	60 15	63 26	66 02
5	11 19	21 48	30 58	39 40	45 00	50 12	54 29	58 00	60 57
6	9 28	18 26	26 34	33 41	39 48	45 00	49 24	53 08	56 19
7	8 08	15 57	23 12	29 45	35 32	40 36	45 00	48 49	52 08
8	7 11	14 02	20 33	26 34	32 00	36 52	41 11	45 00	48 22
9	6 20	12 32	18 26	23 58	29 03	33 41	37 52	41 58	45 00

Table II. Latitude of Plane (*HKL*)

Latitude is positive when H is positive and negative when H is negative.
Latitude = 0° for all planes that have $H = 0$.

$K^2 + L^2$ \ H	1	2	3	4	5	6	7	8	9
0	90°00′	90°00′	90°00′	90°00′	90°00′	90°00′	90°00′	90°00′	90°00′
1	45 00	63 26	71 34	75 58	78 41	80 32	81 52	82 55	83 39
2	35 16	54 44	64 46	70 32	74 13	76 44	78 34	79 59	81 04
3	26 58	48 00	58 19	65 26	69 12	71 34	74 03	75 58	77 28
4	24 06	41 48	53 16	60 47	65 54	69 14	72 17	74 23	76 05
5	19 28	35 16	46 31	54 44	60 15	64 46	68 36	70 32	72 33
6	18 26	33 41	45 00	52 08	57 32	61 56	65 28	68 12	70 39
7	17 33	32 19	43 40	51 40	56 13	59 00	62 43	65 26	68 10
8	15 00	29 03	39 47	47 33	51 20	56 19	60 15	63 26	66 02
9	14 02	26 34	36 52	45 00	51 20	56 19	60 15	63 26	66 02
10	13 16	25 14	35 02	44 08	50 29	55 30	59 08	62 44	65 26
11	13 16	25 14	35 16	43 19	49 41	54 44	58 47	62 04	64 46
12	12 26	24 06	33 51	41 40	48 11	53 18	57 23	60 47	63 35
13	11 19	21 48	30 58	39 40	45 00	50 12	54 28	58 00	60 57
14	11 06	21 25	30 20	38 05	44 26	49 38	53 56	57 29	60 28
15	11 31	20 22	29 07	36 36	42 53	48 06	52 26	56 53	59 58
16	10 01	19 28	27 36	35 16	41 28	46 41	51 04	54 44	57 51
17	9 44	18 53	27 13	34 27	40 37	45 49	50 12	53 55	57 04
18	9 20	18 12	26 15	33 20	39 25	44 36	49 01	52 45	55 57
19	9 00	17 33	25 23	32 19	38 20	43 28	47 54	51 42	54 54
20	8 59	17 33	25 23	32 19	37 59	43 08	47 33	51 20	54 34
21	8 55	17 21	25 06	32 00	38 42	41 48	46 13	50 01	53 18
22	8 29	16 46	24 06	30 48	35 16	40 19	44 43	48 32	51 51
23	8 03	15 48	22 59	29 30	34 44	39 47	44 09	47 58	51 18
24	7 54	15 30	22 35	29 01	34 29	39 30	43 53	47 42	51 02
25	7 50	15 22	22 24	28 47	33 17	38 14	42 35	46 25	49 46
26	7 29	14 43	21 30	27 43	33 17	38 14	42 35	46 25	49 46
27	7 18	14 22	21 01	27 07	32 38	37 32	41 52	45 41	49 03
28	7 04	13 56	20 24	26 25	31 48	36 39	40 58	44 47	48 09
29	6 59	13 46	20 11	26 09	31 18	36 02	40 20	44 08	47 30
30	6 43	13 16	19 28	25 14	30 31	35 16	39 31	43 19	46 51
31	6 41	13 10	19 21	25 05	30 20	35 05	39 18	43 07	46 39
32	6 39	13 05	19 14	24 56	30 16	34 54	39 08	42 55	46 18
33	6 23	12 36	18 32	24 06	29 38	34 01	38 03	41 48	45 11
34	6 18	12 27	18 20	23 50	28 58	33 32	37 42	41 28	44 49
35	6 11	12 14	18 02	23 27	28 28	33 03	37 12	40 57	44 19
36	6 03	11 58	17 38	22 59	27 55	32 25	36 25	40 18	43 39
37	6 01	11 54	17 33	22 52	27 47	32 10	36 23	40 08	43 30
38	5 48	11 29	16 56	22 06	26 55	31 21	35 24	39 05	42 25
39	5 47	11 25	16 51	22 00	26 48	31 13	35 16	38 57	42 17
40	5 43	11 19	16 42	21 48	26 34	30 58	35 00	38 40	41 59
41	5 33	11 06	16 15	21 14	25 54	30 14	34 13	37 51	41 10
42	5 22	10 39	15 46	20 40	25 11	29 27	33 22	36 58	40 15
43	5 17	10 29	15 30	20 18	24 48	29 01	32 55	36 29	39 47
44	5 03	10 01	14 51	19 28	24 01	27 56	31 45	35 16	38 30
45	5 01	9 57	14 44	19 20	23 51	27 45	31 33	35 03	38 17
46	4 45	9 26	14 04	18 29	23 43	27 30	31 16	34 46	38 00
47	4 43	9 22	13 59	18 23	22 55	26 39	30 19	33 36	36 46
48	4 30	8 56	13 36	17 27	21 27	25 14	28 49	32 09	35 16

following are examples of longitudes and latitudes obtained from these tables:

(*HKL*)	Longitude	Latitude
(111)	45° 00′	35° 16′
(257)	35° 32′	13° 05′
(752)	68° 12′	32° 26′
(968)	48° 22′	36° 46′
(119)	6° 20′	6° 18′

If a polar stereographic net is used instead of a Wulff net, the tables can be used to find φ and θ, Fig. 2.

$$\varphi\ (HKL) = \text{Longitude}\ (LKH)$$
$$\theta\ (HKL) = 90° - \text{Latitude}\ (LKH)$$

For example:

φ (112) = Longitude (211) = 45° 00′
θ (112) = 90° − Latitude (211) = 35° 16′
φ (129) = Longitude (921) = 63° 26′
θ (129) = 90° − Latitude (921) = 13° 57′
φ ($\bar{5}31$) = Longitude ($13\bar{5}$) = 210° 58′
θ ($\bar{5}31$) = 90° − Latitude (135) = 80° 16′

Appendix

The tables have been calculated on the basis of the following relations which can be derived by use of simple trigonometry:

$$\text{Longitude}\ (HKL) = \text{Arc tan}\ \frac{K}{L}$$

$$\text{Latitude}\ (HKL) = \text{Arc tan}\ \frac{H}{(K^2 + L^2)^{1/2}}.$$

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[1] E. Schiebold and G. Sachs: *Ztsch. Krist.* (1926) **63**, p. 34.

[2] C. S. Barrett: *Structure of Metals*, Chapter 2 (1943) New York: McGraw-Hill Book Co.

Sampling of Liquid Steel for Dissolved Oxygen

(With Discussion)

An improved bomb sampling technique for obtaining samples for oxygen analysis from liquid steel is described. Analyses of samples taken from open-hearth furnaces by the improved method show sufficient agreement with laboratory data to indicate the accuracy of the method is better than that of other existing sampling methods.

THE bomb-sampling method of determining the oxygen content of a liquid-steel bath was studied by obtaining and analyzing more than 200 samples from normal open-hearth heats. Of these samples, about 60 were obtained with a bomb of conventional design, the remainder were taken with a somewhat modified bomb designed to give greater protection against slag contamination. In the new device, the contacting faces of the cast-iron mold halves are machined so that they fit closely, the opening at the top of the bomb is covered with a thin steel cap, and the top of the bomb is further covered with a wood block held in place by heavy steel wire. After the bomb has passed through the slag layer and has entered the steel bath, the wire melts and the wood block floats to the surface. Thereafter, the steel melts through the thin cap and flows into the bomb cavity where it is deoxidized with aluminum wire. An assembled bomb, ready for sampling, is shown in Fig. 1.

To standardize sampling procedures, the samples were usually taken through the center door and at the bottom of the furnace, that is, the bomb was on the bottom when the metal cap melted. After each addition to the furnace, at least 20 min elapsed before a sample was taken.

The oxygen contents of all the samples were determined by using the vacuum-fusion method, two or more specimens from each sample being analyzed. The specimens were cubes of metal cut from a region in the interior of the bomb sample, as shown in Fig. 2. Drillings for carbon analysis were obtained immediately above the oxygen-analysis region.

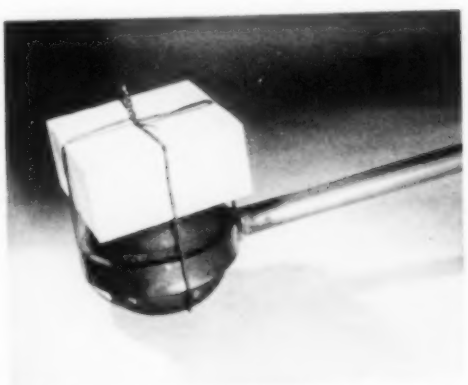

Fig. 1—Modified bomb assembled and ready for sampling.

Reproducibility of Results

In determining the reproducibility of the results obtained with the modified bomb, the following four factors were studied: 1—variation in the oxygen concentration of duplicate specimens taken from a single sample; 2—variation in the oxygen concentration of duplicate samples taken in quick succession; 3—effect of the amount of aluminum wire

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which was used as a deoxidizer on the oxygen concentration of samples, and 4—effect of the size of aluminum wire.

Analyses of specimens from each bomb sample showed that, for two thirds of the samples, the oxygen concentrations of the two or more specimens differed from each other by less than 10 pct of the mean oxygen concentration; for seven eighths of the samples, by less than 15 pct; and for only one twentieth of the samples, by 20 pct or more. Because of this good agreement, the extent of segregation of alumina particles was not considered significant; consequently, segregation was eliminated as a possible source of any discrepancy between the actual oxygen content of the bath and that of the bomb sample.

The data for the duplicate samples taken in quick succession were gathered on the assumption that should errors in the oxygen determination arise from such sources as slag entrapment or a boil on the cold surfaces of the bomb, the oxygen analyses of the pair would probably not agree. The carbon and oxygen contents of the duplicate samples are shown in Table I. Of the 19 pairs of samples, 12 (63 pct) show a difference in oxygen content of 0.001 pct or less; 16 (84 pct), a difference of 0.002 pct or less; 17 (90 pct), a difference of 0.003 pct or less. This compares favorably with the precision claimed by Brower and Larsen[5] for their spoon method.

Derge, in his work with the wedge-sampling method,[2] reported oxygen data on 15 duplicate samples. Of these, two showed a deviation as high as 0.013 pct oxygen, and eight as high as 0.0045 pct.

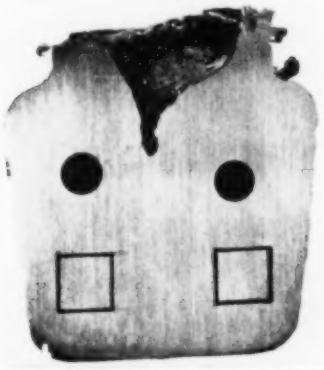

Fig. 2—Sample ingot showing positions from which specimens for vacuum-fusion analyses (square areas) and carbon analyses (round holes) were taken.

Fornander[1] took bomb samples with a device exactly the same as that described in the present paper except that the molds were machined from mild steel rather than from cast iron. He reports that of 39 duplicates, only one pair showed a discrepancy larger than 0.003 pct O. There is no indication, however, that Fornander took any of these samples from baths having carbon contents of less than 0.04 pct.

The amount of aluminum wire added to approximately half the samples was 0.5 pct of the sample weight; the amount added to the remainder was 1.0 pct. Fig. 3 shows that either of these percentages is satisfactory provided that the vacuum-fusion method is used in analyzing the specimens.

Table I. Carbon and Oxygen Contents of Duplicate Samples Taken With the Modified Bomb

Sample No.	C, Pct	O, Pct	Sample No.	C, Pct	O, Pct	Sample No.	C, Pct	O, Pct
B-564	0.34	0.0127	B-629	0.13	0.0238	B-42	0.41	0.0111
B-565	0.34	0.0137	B-630	0.13	0.0240	B-43	0.41	0.0142
B-566	0.22	0.0163	B-631	0.12	0.0230	B-44	0.27	0.0155
B-567	0.22	0.0172	B-632	0.12	0.0216	B-45	0.27	0.0161
B-568	0.34	0.0135	B-633	0.46	0.0150	B-46	0.052	0.0462
B-569	0.34	0.0136	B-634	0.46	0.0129	B-47	0.052	0.0483
B-570	0.22	0.0195	B-635	0.24	0.0178	C-638A	0.022	0.069
B-571	0.21	0.0202	B-636	0.21	0.0169	C-638B	0.031	0.070
B-637	0.32	0.0120	B-675	0.67	0.0120	C-639A	0.024	0.070
B-638	0.32	0.0109	B-676	0.67	0.0120	C-639B	0.028	0.075
B-440	0.22	0.0211	B-638	0.49	0.0130	C-766A	0.014	0.0510
B-441	0.21	0.0205	B-640	0.49	0.0127	C-766B	0.014	0.0505
						C-1378A	0.041	0.0360
						C-1378B	0.032	0.0345

The size of aluminum wire might have an effect on the reproducibility of results because, for very small wire, the surface-to-volume ratio is sufficiently large that the normal aluminum oxide film on the wire might introduce a significant error in the oxygen determination. On the other hand, wire of large diameter may not be completely melted before the steel solidifies and consequently may not be distributed uniformly throughout the sample. In the series of samples taken with the conventional bomb, wire diameters of 0.012, 0.050, and 0.081 in. were used so that any difference in the oxygen analysis due to the size of aluminum wire could be detected. Fig. 4 shows that the size of aluminum wire has no significant effect on the results. There is no reason to suppose that this finding would be changed by the use of the modified bomb. Actually, in the modified-bomb series, wires with 0.012 and 0.050 in. diameters were used interchangeably.

How representative the results of the vacuum-fusion analyses of bomb samples are of the actual oxygen concentration in the liquid-steel bath can be inferred only from the usefulness of the data in understanding the reactions that occur in the bath.

Carbon-Oxygen Reaction

In Figs. 3 and 4, the data obtained with the modified bomb and with the conventional bomb, respectively, are plotted as activity of oxygen vs. weight percentage (activity) of carbon. Laboratory experience has shown that the activity coefficient of carbon does not differ much from unity except at carbon concentrations greater than 1 pct. Consequently, the carbon activity for all the samples was considered equal to the weight percentage of carbon. The values for activity of oxygen were obtained by multiplying the percentage of oxygen by the activity coefficient of oxygen determined by Marshall and Chipman.[6]

In Fig. 5, average curves are plotted for three methods of sampling; namely, the modified-bomb method, the conventional-bomb method, and the Brower and Larsen spoon method. For comparison, the equilibrium curve for a pressure of 1.6 atm (36-in. bath depth) and an average open-hearth temperature of 1577 C (2870 F) is plotted as a dashed line.[7]

The data obtained with the modified bomb is represented by curve 2 in Fig. 5. For carbon con-

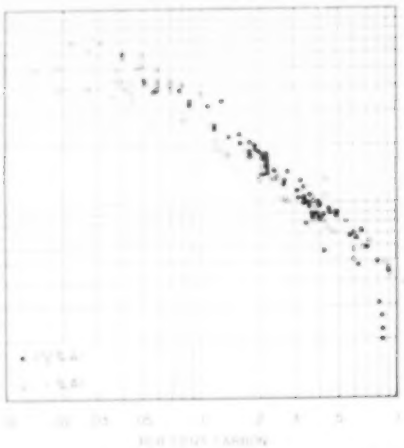

Fig. 4—Oxygen activity vs. percentage of carbon—modified bomb

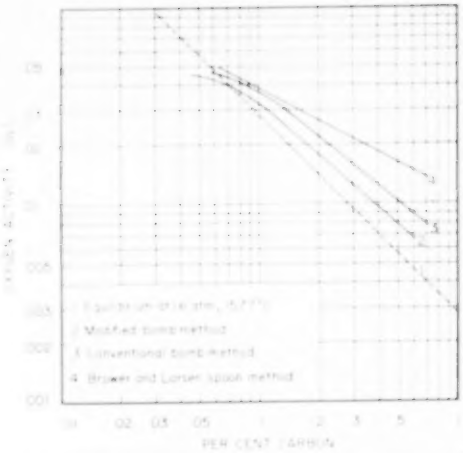

Fig. 5—Oxygen activity vs. percentage of carbon—comparison of various methods of sampling

centrations greater than about 0.08 pct, curve 2 lies somewhat above equilibrium curve 1. This difference in the position of the two curves is expected, since a concentration of oxygen in excess of the equilibrium concentration is required to permit the carbon-oxygen reaction to progress at a practical rate (Brower and Larsen 301). But it must be emphasized that the exact amount of excess oxygen required is not known, and that at least part of the difference in the position of the two curves may be due to a systematic error in the method or to a wrong choice of an equilibrium pressure of 1.6 atm. At carbon concentrations below about 0.08 pct, curve 2 levels off and falls below the equilibrium curve. This condition apparently arises from the fact that the oxygen activity in the metal is now being controlled by the slag rather than by the carbon concentration. Evidence for this hypothesis will be given later.

Fig. 6—Oxygen activity vs. percentage of carbon—conventional bomb

The curve representing the data obtained with the conventional bomb, curve 3, Fig. 5, shows the same general behavior as the curve for the modified bomb. However, the oxygen values obtained are higher in the former method. The difference may be attributed to the presence of slag in the samples taken with the conventional bomb, although an effort was made to keep slag off the metal cap while slagging the bottom and the sides of the bomb. This effort may not always have been entirely successful; or, if the effort was successful, slag may have adhered to the cap a few seconds later when the whole assembly was plunged through the slag layer into the metal. When the cap was subsequently melted, this small amount of slag would have been washed into the bomb cavity where the oxides of iron, manganese, and silicon would have immediately oxidized the aluminum to aluminum oxide. Consequently, the analysis for oxygen, whether performed by using either the vacuum-fusion method or the wet chemical method, would have given high results. A number of samples taken with this method were discarded without analysis because of large slag inclusions, Fig. 6. The wood cover used on the modified bomb prevented contact between the slag and the top of the bomb.

Data obtained by Brower and Larsen with their spoon method are represented by curve 4, Fig. 5. The oxygen concentrations obtained with this method are considerably higher than those obtained with either of the bomb techniques. The possibility that the high oxygen values are caused by pouring the liquid metal through the air is immediately suggested. In the bomb method, of course, the sample is solid before it comes in contact with air.

Equilibrium Between Slag and Metal

Curves 2 and 3 of Fig. 5 both show a tendency for the oxygen activities to level off at low carbon concentrations. It appears that when the carbon content is below about 0.10 pct, it no longer controls the oxygen concentration. This observation implies that in the finishing stage of a low carbon heat, the oxygen concentration depends on the oxidizing power of the slag; for, although the carbon present will

allow a higher oxygen value than is actually found, the steel can have no higher oxygen pressure than the slag, which is its only source of oxygen.

The tendency toward equilibrium of slag and metal may be verified by making use of recent work of Herasymenko.[7] This author has derived empirically the following equation from the laboratory data of Winkler and Chipman:[8]

$$A(O^{--}) = \frac{(Fe^{++})(O^{--})}{[a_o]}$$

$$\text{or } A = \frac{(Fe^{++})}{[a_o](O^{--})^{1/2}}$$

where (Fe^{++}) is the ion fraction of ferrous ion in the slag; (O^{--}), the ion fraction of oxide ion in the slag; $[a_o]$, the activity of oxygen in the metal; and A, a constant.

Slag samples were taken simultaneously with nearly 50 of the modified-bomb samples. The data thus obtained were substituted into the equation just referred to in order to obtain A. In Fig. 7, A is plotted against the logarithm of carbon concentration. Reference to this graph shows that A is certainly not constant at carbon levels greater than 0.10 pct but tends toward a constant value at the lower carbon levels.

Summary

An improved bomb-sampling device for the sampling of liquid steel for dissolved oxygen is described. The improvements are all designed to provide better protection against slag contamination than that afforded by the conventional bomb. It is shown that the oxygen analyses obtained with the vacuum-fusion method are consistent both within a single sample and between duplicate samples.

The effect of the amount and the size of aluminum wire used as a deoxidizer is shown to be insignificant within the ranges studied.

The relationship of the oxygen concentration of an open-hearth bath to the carbon concentration and to the slag composition is considered; and it is shown that the oxygen dissolved in the bath is more nearly in equilibrium with the carbon at carbon levels greater than 0.10 pct and is more nearly in equilibrium with the slag at carbon levels less than 0.10 pct.

Fig. 6—Sample obtained with conventional bomb showing slag entrapment.

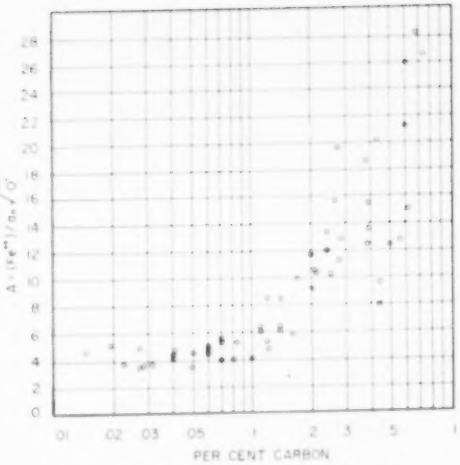

Fig. 7—Oxygen equilibrium between slag and metal.

Acknowledgments

The authors wish to express their appreciation to the personnel of the Homestead District Works, Duquesne Works, and Vandergrift Works of the United States Steel Co. whose cooperation and helpfulness made this work possible.

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[2] T. E. Brower and B. M. Larsen: *Trans.* AIME (1945) **162**, p. 712.

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[6] Herasymenko and Speight: *Journal* Iron and Steel Inst. (1950) **166**, Part 3, p. 169.

[7] T. B. Winkler and J. Chipman: *Trans.* AIME (1946) **167**, p. 111; METALS TECHNOLOGY (April 1946).

DISCUSSION, D. L. McBride and R. E. Birch presiding

C. R. Taylor (*Armco Steel Co., Middletown, Ohio*)—We have conducted investigations along quite similar lines, and our results agree very well with those presented by Dr. Huff.

In the low carbon end of the diagram, Fig. 3, there is an effect of manganese on oxygen solubility. When carbon contents are less than 0.06 pct, the manganese can have an effect. If a manganese "correction," if you want to call it that, is applied, the scatter, pct O vs. the reciprocal of the carbon content, is considerably diminished.

We have used a small wooden plug, preferably of soft wood, occasionally in the bomb test, instead of a metal cap, which is inserted into the top of the mold. As soon as it is charred a little bit, it blows out and allows the metal to go into the mold, and the results appear to be good when it is used.

I would like to ask Dr. Huff what chemical method is used to determine the alumina content of the sample. I do not believe he mentioned that.

G. F. Huff (authors' reply)—All oxygen analyses reported were determined by the vacuum-fusion method.

Dr. Taylor—That would apply to the solid piece, but you had drillings, too.

Dr. Huff—Those drillings were for carbon. We did not use a wet chemical method for the determination of alumina.

Dr. Taylor—We have used straight nitric acid for solution of millings or drillings with good results.

R. M. Larsen (*United States Steel Co., Kearny, N. J.*)—The authors of this paper have done a very careful and painstaking job in refining of analytical methods and in checking duplicate samples obtained by the method of sampling which they have developed, and my only reason for being critical of this paper is that I believe there is good reason to believe that this method of sampling in general gives low results. This matter is of some importance because our picture of the mechanism of this whole process, of the carbon oxidation reaction, of the movement of oxygen into the liquid steel, and of the sort of equilibrium or steady state which exists between slag and metal, all these are affected more or less by this question of the degree of supersaturation of oxygen in the bath with respect to any given level of carbon content and effective CO pressure.

Not only the authors of this paper, but most of the other investigators in this problem have apparently taken it more or less for granted that the so-called spoon method of sampling gives high results and it is therefore necessary to use some form of the bomb method to obtain a more precise value, in sharp disagreement with a rather detailed study of the two methods described by Brower and Larsen.[1] Perhaps it has been taken for granted that oxygen from slag or atmosphere will diffuse quite rapidly into the fairly quiet but small mass of steel in the sampling spoon. Actually, however, the rates of diffusion of solute atoms in liquid iron without stirring are of the order of 1 cm per hr, so that, in the approximately 3 to 4 sec required after dipping to remove a spoon and pour the metal, with relatively little mass stirring in the spoon and only 2 to 3 in. of flow distance through the air, the amount of oxygen absorption should be small. This was confirmed in the work previously mentioned,[1] which indicated that, although a small error on the high side was possible with the best spoon-sampling technique, its magnitude could not be greater than about 0.005 pct O and probably was much smaller on the average.

On the other hand, many indications confirm the danger of getting too low a value, due to a localized boiling out of both carbon and oxygen as CO. This will often happen even in the spoon sampling method, if the spoon is not well coated with slag, if the slag is lumpy, or if the metal is cold and starts to freeze in the spoon. This effect has been repeatedly proved by the accompanying loss of carbon wherever there is even a little bit of boiling in the spoon before the metal can be poured into the mold containing aluminum wire. In general, whenever we were sampling on a cold bath or one with lumpy slag, or if any boil in the spoon was suspected on one sample, we would take three check samples, and in a number of such cases, two of the three would check closely in both carbon and oxygen values with the third running low in both oxygen and carbon, the loss of carbon corresponding (within the limits of error) with the decrease in oxygen as compared to the other two samples. There are other indications of this sort which we will not detail here but which all tend to establish the variable but quite appreciable excess of dissolved oxygen in a bath on a boil, equivalent to an apparent CO pressure of anywhere from 2 to 10 atm, so that the main difficulty in obtaining a good sample here is that of preventing the "boil-out" until the metal can be brought into contact with the aluminum wire deoxidizer. This is less a matter of speed than of avoiding conditions tending to stimulate bubble formation in the mass of metal near or in the sample mold. In a well-slagged spoon, the liquid metal is almost totally enclosed by a liquid slag surface which seems to prevent bubbles from starting to form. In bomb sampling on the other hand, even with most of the bomb surface well slagged, the metal which melts through the thin steel cap and which flows over the inside shoulder of the bomb is in contact with cold metal which is a very good bubble starter, and this we believe is what leads to low results, sometimes erratic. Of course if the boil-out is greater, the excess oxygen will be quickly lowered near to the carbon equilibrium, at around 1.5 atm, and results will tend to be lower but less erratic. This is why we felt that the authors here have been fooled by consistent check values; their use of a wooden block over the mold gives them the very best condition for starting a local boil in that metal entering the mold, a conclusion which tends to be substantiated by the values at low carbon, see Fig. 3, which are even below the apparent C-equilibrium value. Note also in Fig. 5 that this wooden block technique tends to give the lowest results, below those with the conventional bomb technique where boil-out probably occurs but to a lesser extent where the wood block is not present to contact the metal for a short time before it breaks off and floats away (even the "heavy steel wire" holding the wood block in place helps to stimulate the localized boiling action). Fig. 5 shows how the spoon-test values are above those from both bomb-mold techniques, and the writer feels that these higher values, though they may average a little bit on the high side, are much closer to the true oxygen contents in a boiling bath.

In general, our criticism is that though the work described in this paper was carefully done, the particular sampling technique employed was so peculiarly designed to give large errors on the low side that the results are of no significance to our understanding of the open-hearth bath process. We would like to urge that more thoughtful consideration be given to the points discussed above and to the advantages of the spoon-sampling technique.

Frank Norris (*Wheeling Steel Co., Steubenville, Ohio*)—I agree with Mr. Larsen to a certain extent, that is, that the authors have certainly done an excellent piece of work and have reported a very useful investigation. Perhaps the question that I would like to ask might throw some light on the point that Mr. Larsen mentioned. Is the bath ahead of the slag or is the slag ahead of the bath? This action of driving from the slag to the bath all the time means the slag is ahead of the bath, and that is certainly true of the method that at one time was the conventional process of oxidizing heats.

The question I would like to ask is: Have you observed any differences between the samples taken after only an ore addition compared with those taken after oxidizing with lance oxygen?

Dr. Huff—We have no data pertinent to this question, since we purposely refrained from sampling for a half hour after an ore addition.

Dr. Taylor—We have made measurements shortly after boiling oxygen and using a bomb test, and they agreed very well with the carbon equilibrium. In other words, there did not seem to be much displacement. However, we have not done much work on it. I would like to point out that the bomb test is slagged up as it goes into the bath, and the only time that this boil could occur is when the piece of metal goes into the bomb. When we take a sample we use little pillboxes. They have a cap and a base, we use the base. We put the aluminum in the pill box, so that as the steel goes into the mold it hits the aluminum immediately, which would prevent any such boiling from occurring in the sample. In other words, it will be killed immediately.

M. Tenenbaum (*Inland Steel Co., East Chicago, Ind.*)—In answer to Mr. Norris' question, we have taken some random samples immediately following additions

of ore and gaseous oxygen to the open-hearth bath. The samples were taken as conventional bomb tests. At the time that these tests were taken, we felt they were accurate and rather useful. We still have no reason to think otherwise. The analysis of samples taken immediately after an ore addition is quite different than that existing earlier. As would be expected, the oxygen content at that time is quite high, reflecting the process whereby the iron oxide dissolves into the molten metal. We have never been successful in sampling for dissolved oxygen using the slagged spoon technique. Actually I am not too sure that it would be possible to obtain a good test using the slagged spoon during the confused period just following an ore addition.

We have also sampled for dissolved oxygen while gaseous oxygen was being introduced into an open-hearth furnace through a jet. A typical result is as follows:

	Bath Analysis, C	Pct O
Sample No. 1 (Before introducing gaseous oxygen)	0.19	0.027
Sample No. 2 (During introduction of oxygen; samples taken just below jet)	0.05	0.067
Sample No. 3 (After jet has been removed 7 minutes after sample No. 2)	0.11	0.043

These figures show that the dissolved oxygen content in the localized highly active zone just below the jet is very high. The carbon content, however, is just about what would be expected with that oxygen analysis. In other words, a condition exists just below the jet where the carbon content is considerably below the average of the bath, while the oxygen is definitely higher. The relation between the bath carbon and bath oxygen is just about what would be expected in the open hearth.

On removing the jet, the local action subsides somewhat and a sample taken at that time indicates that the carbon and oxygen contents are again averaged out; that is, the carbon content increases and the oxygen content decreases correspondingly.

As stated previously, all of our results have been obtained with the bomb-type sample. The major precaution used in taking samples from a moderately quiet bath is that whenever any boiling action is observed above the immersed bomb, the sample taken is discarded.

Our experience with spoon testing has never been too successful. We have surely never been able to develop the same confidence in the technique as has Mr. Larsen. It should be pointed out, however, that wherever we have had an opportunity to compare results, we have found that our oxygen values have corresponded reasonably well with those of Mr. Larsen.

Mr. Larsen—There was not anything very involved about the spoon-sampling technique, except that we did have to be very fussy about getting a well-sampled spoon. We also found, if we lined the top of the bomb with aluminum foil and then put on a little aluminum cap and had a loose iron cover, just to give a little shielding to get through the slag, that the values were more nearly in agreement with the spoon-test values. Since those values seemed to agree best with the carbon-oxygen drop in tapping, we felt that all that extra trouble in the bomb technique was hardly justified.

Mr. Tenenbaum—We have tried using aluminum caps on our bomb molds. In general, results with the aluminum cap tended to be less consistent and somewhat higher than were the results obtained when using steel caps. We attributed the higher and less consistent results to the observed presence of slag in the tests obtained when using the aluminum caps. We never did shield the aluminum caps. I would expect that the results obtained by Dr. Taylor would come closest to the shielded-cap condition.

Mr. Larsen—The main thing that we concluded was that the bath has a boiling tendency, and when the metal has to melt through any steel cover or cap in getting through the mold cavity, that is the time in which it can do a little boiling, even on only a very thin layer of steel. The impression that we formed was that in such a boiling bath (and a steady state carbon boil indicates a bath which has a very natural tendency to boil), any such condition you put in there, your chances of getting too low will be greater than getting high.

Robert Kulp (*Electro Metallurgical Co., Pittsburgh*)—Mr. Larsen once presented a very nice paper on air oxidation of various elements in the tapping of open-hearth heats. I cannot see on the basis of those results how it can be argued that this spoon test is proper, because in pouring that spoon test you do expose your steel to the atmosphere.

P. Herasymenko (*New York University, New York*)—I concur with the opinion expressed by Mr. Larsen that the reproducibility of tests does not constitute the proof that the test method is correct. It is usually assumed that the composition of the steel bath remains unchanged when the bomb sampler is immersed in the boiling bath. A very simple experiment can be made to prove that a considerable change in the composition of the liquid metal can take place during the immersion of solid metallic bomb.

Take a very thin sheet which is used for the cap of the bomb, immerse it for a fraction of a second, say half a second, into unkilled liquid steel which is contained in an induction furnace without slag. During this very short immersion, we observe a very rapid evolution of gas on the sheet. When this sheet is withdrawn from the bath after half a second of immersion, we observe that the sheet remained unmelted, and about 1 mm of steel has solidified on each side of this very thin sheet.

In the case of the bomb, the mass of metal is much larger so that more steel can solidify on the cap before it is remelted again. The solidified steel and the cap itself act as excellent catalyzers for the carbon-oxygen reaction. Thus, there must be some decrease in the oxygen content of steel entering the bomb.

The fact that the method used by Brower and Larsen gives higher oxygen values speaks in favor of their method. This can be proved easily by taking samples for oxygen determination by both methods before and immediately after the addition of a strong deoxidizer, say ferrosilicon, to a boiling bath containing high carbon. We observe that before the addition, the bomb samples give much lower, sometimes twice lower, oxygen contents than the spoon samples. On the other hand, spoon samples taken shortly after the deoxidation of liquid steel with ferrosilicon give practically identical oxygen values with those found in bomb samples. Thus, it can be concluded that the oxygen pickup in spoon samples from the air and from slag coating of the spoon can be neglected.

I think that the danger of extraneous oxidation of steel in the spoon is exaggerated. The spoon method is simpler and, when the operator has acquired sufficient skill, is quite as reproducible as other more complicated methods.

Shadburn Marshall (*United States Steel Co., Pittsburgh*)—I would like to say a word or two in defense of Dr. Huff. He set out to evaluate a bomb method and that is all he has reported here. In his evaluation of it, to determine its precision, he took duplicate samples. The results he obtained on duplicate samples are closer than those anybody else has reported by the spoon method. I would say that that shows better precision. It is the only means we have to determine the precision. Then he proceeds to determine as nearly as he can the accuracy of the method. He picks the carbon-oxygen equilibrium data, and the results by his bomb method approach that closer than those of any other method based on data in the literature.

Discussion—Iron and Steel Division*

New York Meeting, February 1952

A Corrected CO/CO_2 Ratio for Blast Furnaces (paper by S. T. Killian, JOURNAL OF METALS, September 1951, p. 742) 1168

Distribution of Manganese and Oxygen Between Molten Iron and FeO-MnO-SiO_2 Slags (paper by H. B. Bell, A. B. Murad, and P. T. Carter, JOURNAL OF METALS, July 1952, p. 718) 1172

Silicon-Oxygen Equilibrium in Liquid Iron (paper by N. A. Gokcen and J. Chipman, JOURNAL OF METALS, February 1952, p. 171) 1174

Sampling of Liquid Steel for Dissolved Oxygen (paper by G. F. Huff, G. R. Bailey, and J. H. Richards, This issue, p. 1165)

* TP 3391C

A Corrected CO/CO_2 Ratio for Blast Furnaces

By [illegible]

DISCUSSION, Simon Forgeshaum presiding

T. L. Joseph (*University of Minnesota, Minneapolis, Minn.*): Mr. Killian is to be commended for his inquiry as to why a decrease of 15.3 pct in coke consumption was accompanied by a decrease of only 1.9 pct in the CO/CO_2 ratio of the top gas. Although I encouraged him in his efforts to find a more significant and meaningful carbon-gas ratio, the method, calculations, and conclusions originated entirely with the author. Whether we agree entirely with the assumptions underlying his corrected ratio, I think we can all agree that a better ratio is needed, and that he deserves credit for recognizing the need and for doing something about it.

To be most useful, the CO/CO_2 ratio for the top gas should reflect the way in which the carbon is gasified in the furnace, particularly the degree of oxidation and the extent of heat release. The effect of CO_2 from the decomposition of the limestone and the effect of the reaction of CO and water vapor in the upper part of the furnace on the quality of top gas should be isolated from the effect of more basic reactions such as ore reduction and solution loss.

The reduction of sufficient iron oxide to produce a ton of pig iron and the accompanying changes in the proportions of the carbon gases can be expressed on a mol basis as follows:

$$16.5Fe_2O_3 + 16.5CO = 33FeO + 16.5CO_2 \quad [1]$$

$$33FeO + 33.0CO = 33Fe + 33CO_2 \quad [2]$$

The CO_2 from eq 1 normally escapes from the furnace because it does not react with coke at the temperature of its release. However, as much as 50 pct of the CO_2 from eq 2 may react with coke because it is released at temperatures above 1000 C:

$$16.5CO_2 + 16.5C = 33CO \quad [3]$$

Thus we see that the gasification of 16.5 mols or about 200 lb of C in solution loss will regenerate as much CO as is required for the last stage of reduction. The pronounced effect of reaction 3 on the final proportions of CO and CO_2 in the gas stream is obvious. It also follows that reaction 3 materially alters the heat release but it cannot be entirely eliminated in Lake ore practice. A previous study indicates that 100 lb of solution loss may be necessary to maintain the reducing power of the gas. A reduction of 100 lb from the normal level of 200 lb would mean that over 1,000,000 additional Btu are released in the process. The 100 lb of additional carbon which will be burned at the tuyeres will release 437,000 Btu and the absorption of 583,000 Btu by eq 3 would be prevented.

Table IX. Hydrogen Pickup on Four Levels Above the Tuyeres

Plane No.	Ft Below Stockline	Ft Above Tuyeres	H_2, Pct	H_2 Accumulative, Pct	Average Temperature, F
1	5	65	2.4	72.0	700
2	11	57	2.2	64.4	1200
3	21	46	2.5	54.0	1570
4	44	24	6.9	30.7	1520
Tuyeres	68	0	1.37	27.0	

One of the chief objectives of sized ore burdens and more uniform distribution of the gas stream is to minimize solution loss by completing reduction higher in the furnace and in turn to release the maximum amount of heat from the carbon charged. It was odd, indeed, to find that the use of sized ore and sinter in the careful tests reported by Dobscha had changed the CO/CO_2 ratio very little.

The author has stressed the close correlation between his corrected CO/CO_2 ratio and production. A correlation of fuel consumption and the CO/CO_2 might be more logical. Fuel consumption on the prepared ore burden decreased 15.3 pct whereas the corrected CO/CO_2 ratio decreased 19.0 pct. Although this agreement between the reduction in fuel and the reduction in corrected CO/CO_2 ratio is not as close as the correlation with tonnage, it indicates the corrected ratio is superior to the normal ratio which decreased less than 4 pct.

Some adjustment should be made for the reaction:

$$CO + H_2O = CO_2 + H_2 - 700Btu \quad [4]$$

because there is evidence to indicate that about one half of the hydrogen is formed in the upper 21 ft of

the stock and about 28 pct in the upper 3 ft of the stock.

In exploring the gas phase of a Lake ore furnace at four levels above the tuyeres, Kinney[7] obtained the information on hydrogen pickup given in Table IX.

The top gas from this furnace contained 4.1 pct H_2 equivalent to a pickup of 28.2 pct in the upper 3 ft of the stock. Evidently, water added to the skip to control dust losses promotes the formation of hydrogen. At temperatures below 1600°F, 54 pct of the hydrogen was formed in the upper 21 ft of the stock. Reaction 4 is endothermic and accordingly proceeds to the right at lower temperatures. Moreover, it is highly susceptible to catalysis by iron oxides. However, 27 pct of the H_2 was formed at the tuyeres by way of moisture in the blast and the water-gas reaction. Therefore, we cannot assume that all of the hydrogen in the top gas is formed by reaction 4. Before we can adjust the CO/CO_2 ratio for H_2, we need more complete information as to what portion of the total H_2 is formed by reaction 4.

Rather than make no correction at all, I think it would be better to assume that perhaps 65 to 75 pct of the H_2 is formed by reaction 4. Certainly changes in the CO/CO_2 rates as a result of this slightly endothermic reaction are far less significant than changes resulting from reaction 3.

J. F. Elliott (*Inland Steel Co., East Chicago, Ind.*)—The author has attempted to reinstate the CO/CO_2 ratio as a guide to blast-furnace performance. Certainly all readily obtained data from a furnace should be squeezed of their information to give an operator the maximum aid in running his furnace.

The paper contains a simplified, perhaps overly so, evaluation of the performance of CO_2 liberated from limestone well down in the furnace and of water vapor entering with the charge. The treatment presented has several basic underlying assumptions; one of which is that all the hydrogen formed at or near the top of the furnace results from the homogeneous water-gas reaction:

$$H_2O + CO \rightleftarrows CO_2 + H_2 \qquad [5]$$

It is well known that generally gas-solid reactions proceed more rapidly than gas-gas reactions. Therefore, it might be expected that reaction 6 would prevail over reaction 5:

$$H_2O + C \rightleftarrows CO + H_2 \qquad [6]$$

Or that there might be a combination of eq 5 and:

$$CO_2 + C \rightleftarrows 2CO \qquad [7]$$

In either case the net result is the same and it is probable that there is a lesser tendency to form CO_2 than CO. If CO from oxidation of carbon by the water of hydration could be tagged, probably farther up in the furnace some of it would be found converted to CO_2 by the reverse of eq 7, by reaction with ore, or by reaction with water vapor.[5] The point to be made is that, as a net result of reduction of water in the burden to H_2, some CO as well as CO_2 is formed directly or indirectly. (All of the possible equations have not been listed.) Unfortunately there seems to be no means of fixing the ratio of CO to CO_2 formed from water reduction. The controlling conditions in a given furnace probably are ever changing. Perhaps the only thing that can be stated with reasonable certainty is that the normally burdened furnace (Table X) has the larger quantity of water of hydration in its burden and a higher top temperature than does the furnace with the beneficiated burden. Consequently it should show a greater amount of H_2 from the burden in its gas. This it does having 5.8 lb mols per ton of iron compared to 3.1 for the beneficiated burden.

Mr. Killian's method is a reasonable first approximation for correcting the top gas ratio for the reduction of water vapor. It probably results in a sizable over-correction of the CO/CO_2 ratio, the magnitude of which is difficult to establish since it is a function of the highly variable furnace top conditions.

The correction for CO_2 coming from the limestone involves the assumption that it escapes from the furnace untouched by conditions in the furnace. Limestone probably calcines at temperatures above 1400°F and the CO_2 liberated comes in contact with carbon and ore in various stages of reduction. Joseph's[6] calculations estimate that over 40 pct of the CO_2 in this zone is reconverted by solution loss, eq 7, to CO. The chemical path followed by carbon from the limestone is quite uncertain. Some leaves the furnace unchanged as CO_2 and some is converted to CO by eq 7; subsequently this may leave as CO or may be reconverted to CO_2.

The freeing of CO_2 from stone has considerable effect on the reducing capacity of the intermediate gas. Joseph[6] has shown that in certain furnaces some solution loss may be necessary to maintain the reducing capacity of the gas. Consequently increasing the limestone relative to other materials charged in a given furnace may possibly increase solution loss. It may be predicted that for a given number of pound mols of fluxes charged, all else being equal, dolomite should cause less solution loss than does limestone. This is because $MgCO_3$ begins to calcine around 700°F which is some 700° to 900°F lower than the calcination range of $CaCO_3$. It is perhaps unfortunate that such effects

Table X. Moisture in Burden Based on 1 Ton of Hot Metal. Data from Dobscha,[4] Tables 2 and 3

Ore	Normal Burden: Amount	Normal Burden: H_2O, Lb	Normal Burden: Ig. Loss, Lb*	Beneficiated Burden: Amount	Beneficiated Burden: H_2O, Lb	Beneficiated Burden: Ig. Loss, Lb*
Group 5—Normal	2748	302	156			
Group 7—Normal	923	113	46			
Group 5—Coarse				1637	169	77
Group 5—Kitchi				545	21	2
Group 7—Kitchi				936	85	41
Group 7—Conc.				92	92	
Added Water	131	131				
Totals		626	202		347	120
Total moisture	828 lb or 46 mols			467 lb or 26 mols		
H from moisture	5.8 − 2.6 = 3.2 mols			3.1 − 1.4 = 1.7 mols		

* Assumed all water of hydration.

Table XI. Gas Stoichiometry of the Blast Furnace. Based on 1 Ton of Hot Metal. Data Obtained from Dobscha,[4] Tables 5 and 6

Material	Normal Burden: Lb Mols	Normal Burden: Lb Mols O	Normal Burden: Lb Mols C	Beneficiated Burden: Lb Mols	Beneficiated Burden: Lb Mols O	Beneficiated Burden: Lb Mols C
Air oxygen (from N_2)	80.0	160.0		42.6	85.2	
Total CO	80.0	80.0	80.0	70.3	70.3	70.3
Total CO_2	59.9	79.9	59.9	53.2	69.6	53.3
Total H_2	7.4			4.8		
Total N_2	190.0			160.0		
Totals			139.9			123.6
Blast moisture	1.6	1.6		1.4	1.4	
Total O in blast		162.2			86.6	
O in flux	10	20	10	6.8	13.6	6.8
Total C gasified			115.9			96.8
C in gas—C in flux						
Total C gasified at tuyeres			102.2			89.8
Net "solution loss"			13.7			10.2
Pct net "solution loss"			11.8)			10.3)
Top gas temperature		350°F			325°F	

cannot be observed without careful study because of other more significant differences of CaO and MgO as fluxes.

It is of considerable interest to note that the furnace operating on a beneficiated burden, Table XI, has the lower amount of "solution loss". This is in spite of more sinter in its burden, faster driving, and lower gas volume. It is probable that the higher top temperature, more moisture in the burden, and larger flux charge in the normal burden contribute to this condition. Carbon gasified elsewhere than at the tuyeres is solution loss whether it be in the intermediate zone where some benefit is derived in up-grading the reducing gas or in the top by the water-gas reactions where it probably is wholly detrimental to furnace operation.

In summary it may be stated that the author's methods yield a partially corrected CO/CO$_2$ ratio. In most cases they will give too high a ratio. This is because at high temperatures, 1600° to 1900°F, some CO$_2$ from limestone will be converted to CO and at low temperatures near the furnace top, CO as well as CO$_2$ will result from the reduction of water vapor. However, at present we must be satisfied with this first approximation as with our present understanding the chemical kinetics in the furnace reburn are too complex for more precise treatment.

It is probable that the agreement between the ratios of CO/CO$_2$ for the two burdens and the inverse of the production rates which the author uses to justify his correction is somewhat fortuitous as many factors govern furnace performance.

W. O. Philbrook (*Carnegie Institute of Technology, Pittsburgh*).—Mr. Killian has started with the premise that there is something wrong with the CO/CO$_2$ ratio in blast furnace top gas as obtained by analysis, because it failed to reflect a major improvement in blast-furnace performance obtained with beneficiated raw materials. He has developed corrections which he believes will give a useful guide to blast-furnace operators, and has made the significant observation that the hydrogen content of the gas should not be ignored. Any constructive paper which will stimulate discussion and thus lead ultimately to better understanding of the process is a forward step, and Mr. Killian has made a real contribution in this way. Without wanting to detract from the credit due a conscientious job well done, I should like to take issue with Mr. Killian on the grounds that the corrections do not seem chemically sound and that a single example is not sufficient to establish the empirical value of the calculation. Some constructive attempts to explain the points which have troubled Mr. Killian will be offered.

Hydrogen Correction: Mr. Killian has used the reaction

$$CO_2 + H_2 \rightleftharpoons CO + H_2O\,(g) \qquad [8]$$

as a basis for correcting the gas analysis to a "hydrogen-free basis." The equilibrium constant for this reaction is

$$K = \frac{p_{CO} \cdot p_{H_2O}}{p_{CO_2} \cdot p_{H_2}} \qquad [8a]$$

which may be rearranged to read

$$\frac{p_{H_2}}{p_{H_2O}} = \frac{1}{K} \frac{p_{CO}}{p_{CO_2}} \qquad [8b]$$

The equilibrium constant increases with temperature as shown in Table XII.

It is quite reasonable to look upon eq 8 as a "governor" which tends to maintain a balance among the several possible reactions involving the oxides of carbon, iron oxides, carbon, hydrogen, and water vapor. The reaction would tend toward equilibrium until "frozen" by slowness of reaction rate as the temperature falls along the path of gas flow. In spite of catalysis by iron or its oxides, the reaction rate probably becomes insignificant at a lower level in the shaft than is usually penetrated by the free and combined moisture in the charge, which is vaporized relatively close to the stock line. The hydrogen participating in reaction 8 probably comes from the coke and from moisture in the blast, as will be discussed later. Eq 8 does not seem to be useful quantitatively because there is no practicable way of measuring either the water vapor content of the gas or its temperature at the level in the furnace where the tendency toward equilibrium is frozen. If it were possible to get such information, however, the H$_2$/H$_2$O ratio should be just as valid a measure of "unused reducing power" of the gas as the CO/CO$_2$ ratio.

Kinney's data on hydrogen in the gas at various levels, as shown by Dr. Joseph, do not necessarily prove that the hydrogen was formed by reduction of moisture added at the top of the furnace. No moisture contents of the gas at lower levels in the furnace were reported, and there is not enough information for a reliable calculation to show where the hydrogen involved in eq 8 was introduced into the gas stream.

In using eq 8 to "correct" for hydrogen in the top gas, Mr. Killian has completely ignored the water vapor which would result from the assumed reaction. This is an act of self-deception which might be likened

Table XII. Equilibrium Constant for Reaction $CO_2 + H_2 \rightleftharpoons CO + H_2O$

T, K	T, F	K	T, K	T, F	K
800	980	0.1626	1400	2060	2.25
900	1160	0.225	1500	2420	3.09
1000	1340	0.33	1600	2780	3.90
1200	1700	1.42	2000	3140	4.65

Data from Lewis and Von Elbe.[7]

to trading four lead quarters for a bogus dollar bill and then burning the bill. The transaction might relieve the holder of possible embarrassment from possessing counterfeit money, but it would not change the fact that he had suffered a dollar loss on the deal—nor would it help discover the source of the fraud. Mr. Killian's hydrogen correction is, in effect, a procedure for throwing away a valid part of the oxygen content or used reducing power of the gas and not replacing it.

Correction for CO$_2$ from Flux: The role of CO$_2$ from the flux in the furnace reactions is more subtle than Mr. Killian's correction takes into account. The stone does not calcine to any great extent until it reaches a temperature in excess of 1600°F, which is well into the zone of ore reduction. The CO$_2$ from flux will interact in the same way as CO$_2$ formed by reduction of ore to suppress the reduction of ore by CO or participate in the solution loss reaction. Undoubtedly CO$_2$ from the flux has a real effect on the efficiency of utilization of coke carbon as a reducing agent, but this effect can be learned only by a comparison of overall results for the practices in question. There is no thoroughly reliable way to predict what the CO/CO$_2$ ratio in the top gas might have been if the flux charge had been different, because the whole reaction scheme in the shaft would be altered.

Mr. Killian's second correction assumes that the CO$_2$ rides through the furnace without any change and with no effect but to dilute the top gas and "give an illusion that a greater oxidation of carbon is taking place than really occurs." The adverse effect of flux carbonate is real, but the illusion comes in thinking that it can be accounted for by a simple subtraction.

Corrected Gas Ratio Compared with Production Rate: As confirmation of the validity and usefulness of his corrected CO/CO$_2$ ratios, Mr. Killian shows that they are almost exactly in inverse proportion to the daily production rates for two particular trial periods reported by Dobscha.[6] No additional examples from blast-furnace practice are given to substantiate

the claim. In spite of theoretical objections, Mr. Killian's corrections might prove useful on a purely empirical basis, but their validity would have to be confirmed from a variety of blast-furnace practices. Until such verification has been proved, it is suggested that judgment on Mr. Killian's corrections be held open. Their success in a single comparison might be just an interesting coincidence.

Another Interpretation of Dobscha's Data: It is hardly fair to make a broad indictment of another man's careful and well thought out work without at least attempting to offer constructive suggestions toward an alternative solution of the problem concerned. Considerable time and effort has been put into analyzing Dobscha's data to try to learn whether a marked difference in CO/CO_2 ratios for the two test burdens should have been expected, or whether there really is no anomaly to be explained. Only a few of the high spots can be summarized in a discussion of this nature.

The method of attack included an attempt to set up complete material balances for all major elements to learn what the reducing requirements were for each burden and what the reducing efficiency of the furnace was for each test run. It was necessary to calculate the oxygen content of the ores used and to estimate the iron and oxygen contents of other materials for which exact analyses were not given. It was found that the proximate analyses of all the major charge constituents would total between 99.5 and 100.5 pct if the iron in the ores was calculated to Fe_2O_3 and the sinter was calculated to Fe_3O_4. Reasonable estimates were made for composition of slag, flue dust, etc, and verified by an iron balance, which closed about as well as Dobscha's on the basis of "unrecovered metallics." The carbon balance checked exactly with Dobscha's Table 7. (Dobscha's Table 6 is not exactly consistent with his Table 7 because of a minor difference in computing moisture in the blast.)

The important part of the study hinges on the oxygen balance, and here a serious discrepancy arose. Dobscha in his calculations, and Killian by inference in his correction to hydrogen-free basis, have assumed that H_2 in the top gas is formed by reduction of H_2O by C or CO in the shaft of the furnace. When this assumption was made and the hydrogen balance properly adjusted, then the total oxygen input calculated to over 200 lb more than could be accounted for in the output for both the normal and beneficiated burdens. Since top gas samples were taken after the precipitators, it was thought at first that enough CO might have been dissolved in the wet washers to give an apparent gas analysis significantly low in CO and therefore too high in CO and other constituents. A check revealed that a veritable Niagara Falls would have had to flow through the washers to dissolve enough CO to account for the discrepancy in the oxygen balance. It is likely, however, that minor errors were introduced by taking samples for analysis from the cleaned gas because of different solubilities of the components.

Table XIII. Partial Oxygen Balances for Dobscha's Test Practices

Oxygen Input, Lb per Net Ton Pig Iron	Normal Ores	Beneficiated Ores	Difference, Pct
Oxygen in stock from:			
Iron oxide in ores	825	750	−9
Iron oxide in slag, etc	25	20	
Reduction of Si, Mn, P	40	40	
Less oxygen to flue dust (Fe_2O_3)	60	60	
Net oxygen to gas from metallics	830	760	−8
Oxygen in CO_2 from flux	300	203	−32
Oxygen from blast (O_2 + H_2O)	1630	1373	−16
Total oxygen input to gas	2760	2346	−15

The next approach was to make the reasonable assumption that the coke contained a significant amount of hydrogen—more than that remaining in the top gas—so that oxygen was carried in the top gas as H_2O vapor in addition to that simply evaporated in the upper part of the furnace. Calculation showed that about 1.6 to 1.8 pct H was needed in the coke to make the oxygen balance close, which is over 1 pct higher than is likely for normal coking temperatures.

The coke must also have contained small amounts of oxygen and nitrogen, which would result in some error in the air calculations and carbon and oxygen balances. Other discrepancies would be introduced by normal analytical errors and through imperfect estimates of composition of some of the charge materials and the products. It is evident that complete analytical data for all materials are needed for an accurate material balance, and in particular the hydrogen, oxygen, and nitrogen contents of coke may not be neglected.

Table XIV. Comparisons Calculated for Dobscha's Test Practices

Basis: 2000 Lb Pig Iron	Normal Ores	Beneficiated Ores	Difference, Pct
Net oxygen to gas from metallics	830	760	−8
Net coke, lb	1782	1510	−15.3
Lb oxygen from metallics per lb coke	0.46	0.50	+8
Pct of gasified coke carbon which was burned at tuyeres	69.1	69.0	
Pct C from coke burned to CO_2	26.1	27.8	
Pct H from coke burned to H_2O	X	X	

The next approach was to make the reasonable assumption that the coke contained a significant amount of hydrogen—more than that remaining in the top gas—so that oxygen was carried in the top gas as H_2O vapor in addition to that simply evaporated in the upper part of the furnace. Calculation showed that about 1.6 to 1.8 pct H was needed in the coke to make the oxygen balance close, which is over 1 pct higher than is likely for normal coking temperatures.

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The conclusions to follow will be based primarily on calculated oxygen contents for ingoing materials less oxygen carried out as Fe_2O_3 in flue dust estimated to contain 50 pct Fe. No high order of accuracy is claimed. It is believed, however, that the evidence is fairly strong that H_2 in the top gas comes from hydrogen in coke and moisture in the blast dissociated at the tuyeres rather than from H_2O dissociated higher in the shaft at the expense of carbon or CO.

Partial oxygen balances calculated and estimated from Dobscha's data are given in Table XIII, and comparisons derived from the oxygen and carbon balances are summarized in Table XIV. Conclusions and observations are as follows:

1—The beneficiated burden was upgraded not only in physical structure but also chemically, because 8 pct less oxygen had to be removed by reducing gases in the furnace. Much of this difference is accounted for by the sinter. This lower reducing-agent requirement accounted for about half the 15 pct saving in coke with the beneficiated burden.

2—The amount of oxygen removed from the metallics in the charge per unit of coke was about 8 pct greater for the beneficiated ore. This represents the real improvement in chemical efficiency and accounts for the other half of the coke saving.

3—The thermal requirement of the process was lowered enough by the beneficiation of the ores and reduced slag volume to permit a saving in coke from improved chemical efficiency to be realized.

4—Somewhat less solution loss occurred with the beneficiated burden, probably because better gas distribution through the stock caused the ore to be reduced higher in the furnace.

5—A higher proportion of the coke carbon was converted to CO, with the sized and sintered burden in accordance with the higher chemical efficiency. The proportion of hydrogen converted to H_2O is even more indicative of the improved efficiency of the practice with beneficiated ore, as inferred from a comparison of hydrogen contents of the top gas, but no quantitative comparison can be justified because the hydrogen

balance is incomplete. The higher conversion of hydrogen to water vapor for the prepared burden might be explained on the basis that improved gas flow drove off free and combined moisture in the ores higher in the shaft. This would mean that little or no moisture could penetrate low enough in the stack to interfere with the reduction of ore by H_2 at the temperature level where the final gas composition was established.

6—A combination of more carbon gasified by oxygen from ore above the tuyeres plus more CO_2 from flux in the normal burden, resulted in higher $CO + CO_2$ and lower N in the top gas for the normal practice. This is entirely in accordance with Dr. Joseph's observations[7] and is an indirect indication of the relative efficiencies of the processes.

7—A careful analysis of complete material balances for the entire processes not only gives ample evidence of the increased efficiency but shows how it was accomplished. In this example, part of the improvement came from a lowered demand for reducing agent incidental to the physical beneficiation of the ores. The increased efficiency of utilization of carbon as a reducing agent within the furnace has also been demonstrated, in spite of the coincidence that there was little difference in CO/CO_2 ratio in the top gas.

8—A change in CO/CO_2 ratio in the top gas should be a useful indication of efficiency of operation only when the burden and flux charges remain relatively constant. When a number of changes are made simultaneously, it is unrealistic to expect the CO/CO_2 ratio to reflect them all. Some clues as to the quality of performance may be drawn, with caution, from relative proportions of carbon oxides, nitrogen, and hydrogen, but a complete study is necessary to learn the full story of a drastic change in practice. Juggling the top gas ratio by unsound chemistry is not likely to be a satisfactory substitute.

9—Important errors in blast-furnace material and heat balances may result from failure to determine and consider complete analysis of all materials, especially the minor elements in coke.

F. G. Norris (*Wheeling Steel Corp., Steubenville, Ohio*)—The theory which Dr. Joseph has proposed and which the author has so ably developed is well supported by Dobscha's experiment. Further examination of the data suggests that other and perhaps simpler functions of production and gas composition fit Dobscha's results equally well.

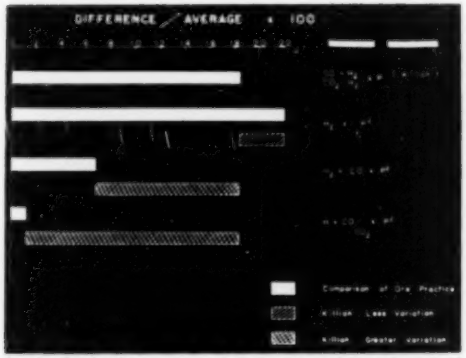

Fig. 1—Graphical comparison of the variation of several proposed functions of blast furnace gas analysis and production.

We have no evidence that shows improved prediction of changes in furnace performance from indications of top gas analysis, but would like to suggest caution in applying relations based on long term averages to predict short range changes as seems to be implied by the reasoning in the third conclusion.

Using Killian's measure of constancy (i.e., the difference divided by the mean) the detailed computations of Table XV are summarized in Fig. 1.

Table XV. Relation of Production to Various Functions of Top Gas Analysis

	Normal Ores	Beneficiated Ores	Average	Difference	Difference/ Average, Pct
(1) Production (net tons per day)	1,324	1,603			
(2) Production equation	1,752,976	2,576,925			
(3) Hydrogen, pct	2.30	1.60			
(4) Product (2) × (3)	4,031,844.8	4,121,640	4,076,742.4	89,795.2	2.203
(5) CO, pct	26.57	26.17			
(6) Product (4) × (5)	107,126,116.336	107,863,318.80	107,494,717.5	737,202.5	0.68
(7) CO_2, pct	12.31	12.40			
(8) Ratio (6)/(7)	86,992,494.9	86,986,547.4	86,934,521.1	104,052.5	0.12

(In the basis of this table, the most nearly constant product is therefore, $4^{0.5} \times H \times CO/CO_2 = 8.69 \times 10^7$ with a saving of 0.12 pct.

In comparing two periods on one furnace having the same general level of total coke, wind, and CO/CO_2 ratio, production varied inversely with the square root of the hydrogen content of the top gas. A more exact relation is that the production squared times hydrogen times CO/CO_2 equals a constant, which for the conditions of Dobscha's experiment is 8.69×10^7.

S. T. Killian (There is no author's reply due to the extended illness of Mr. Killian).

[7] S. P. Kinney: The Blast Furnace Stock Column, U.S. Bur. Mines *T.P.* 442, p. 221.

[7] T. L. Joseph: Solution Loss and the Reducing Power of Blast Furnace Gas, *Trans.* AIME (1951) 191, pp. 37-43; (January 1951 JOURNAL OF METALS).

[7] H. F. Dobscha: Effect of Sized and Sintered Mesabi Iron Ores on Blast-furnace Performance, *Blast Furnace, Coke Oven and Raw Materials Proceedings*, AIME (1948) 7, pp. 49-57.

[8] B. Lewis and G. Von Elbe: *Combustion, Flames and Explosions* (1951), p. 742. Academic Press, New York.

Distribution of Manganese and Oxygen Between Molten Iron and FeO-MnO-SiO$_2$ Slags

by H. E. Bell, A. S. Morrell and F. T. Carter

DISCUSSION, N. J. Grant presiding

N. A. Gokcen (*Michigan College of Mining and Technology, Houghton, Mich.*)—The activities of silica, represented in Fig. 5 for the systems MnO-SiO$_2$ and CaO-SiO$_2$, are in disagreement with the established binary phase diagrams. At $N_{SiO_2} = 0.50$ in MnO-SiO$_2$, and at $N_{SiO_2} = 0.65$ in CaO-SiO$_2$, each binary system is saturated with respect to silica at 1550°C, and therefore a_{SiO_2} is unity in each case. The curves for a_{SiO_2} (FeO-SiO$_2$) and a_{SiO_2} (MnO-SiO$_2$) should nearly co-

incide at approximately $N_{SiO_4^{4-}} = 0.50$, in accordance with the phase diagrams and the investigations of Korber and Oelsen.

It should be pointed out that the slag of this investigation is a complicated four-component system, i.e., FeO, MnO, MgO, and SiO_2, from which the authors obtained the activity values for the simple binary system MnO-SiO_2 after making several assumptions and choosing an entirely arbitrary dotted line as the correct one by ignoring a number of experimental points plotted in Fig. 2. Magnesium oxide was completely ignored as being one of the components, although its concentration varies from 2.1 to 11.1 pct. If it is true, as the authors agree, that CaO affects the activity of MnO in the presence of SiO_2, then the effect of MgO on the activity of MnO cannot be ignored, because CaO and MgO behave similarly in liquid slags. Accordingly, it is difficult to justify that the variation of K'_{Mn} and hence the activity coefficient of MnO can be solely expressed as a function of silica content as in Fig. 2, i.e., assuming that interaction exists only between SiO_2 and MnO, and not MgO and SiO_2 as well as among the four components.

It is tacitly admitted that equilibrium was established between slag and metal in these experiments. Was there any experimental evidence for the attainment of equilibrium, especially in the resistance-heated crucibles in which both metal and slag were static? It is stated that the solidification of 800 to 1000 g of liquid metal, covered with slag in an insulated crucible, required 10 to 15 sec after turning off the power. Was this period of time actually recorded together with the temperature measurements of liquid metal? Our measurements of temperature, with an optical pyrometer sighted on a clean surface of metal under reducing conditions, indicated that 35 g of liquid iron, heated by induction current to 1550°C in 1 mm thick unshielded and uninsulated crucibles, required about 12 sec to freeze after turning off the power. It seems, therefore, impossible to freeze 800 to 1000 g of liquid iron under the conditions prevailing in these experiments in less than a few minutes, after which the retainment of equilibrium without significant changes is questionable.

H. B. Bell, A. B. Murad, and **P. T. Carter** (authors' reply)—The activities of silica shown in Fig. 5 for MnO-SiO_2 are partly based on the results of a recent redetermination of the MnO-SiO_2 phase diagram,[7] which indicates a eutectic between MnO-SiO_2 and SiO_2 at 47 pct SiO_2 and silica saturation (1550°C) at 52 pct SiO_2 ($N_{SiO_4^{4-}} = 0.56$). We apologize for having allowed the a_{SiO_2} line for the CaO-SiO_2 system to tail off incorrectly beyond $N_{SiO_4^{4-}} = 0.6$. As pointed out by Professor Gökcen, $a_{SiO_2} = 1$ at $N_{SiO_4^{4-}} = 0.65$ (1550°C).

The complication of MgO in the slags is one which we would have liked to have avoided. The criticism that we have ignored its possible effect is an important one, and we should perhaps have considered this matter at greater length in the paper. If it is supposed that MgO behaves like CaO in liquid slags, then K'_{Mn} values in the absence of MgO should have been even greater than those actually obtained, and γ_{MnO} and a_{MnO} values lower. It is improbable that the line representing a_{SiO_2} in Fig. 5 would have been lower than a line from $a_{SiO_2} = 1$ at $N_{SiO_4^{4-}} = 0$ to $a_{SiO_2} = 0$ at $N_{SiO_4^{4-}} = 0.33$ (i.e., the corresponding part of the a_{SiO_2} curve). It is not agreed, however, that MgO and CaO behave similarly. Mg^{++} is smaller than Fe^{++}, and its behavior should be more like that of Fe^{++} than that of Ca^{++}.

Further experiments have confirmed the lower curve in Fig. 2. The equilibrium position was approached from both sides. Equilibrium in slag-metal experiments has been reached in 10 min in a similar resistance furnace.

The 10 to 15 sec solidification time refers to the time required for the thin slag layer and iron surface to freeze and not to the freezing of the main body of metal.

K. Grjotheim (*Norwegian Institute of Technology, Trondheim, Norway*)—This paper gives some accurate measurements on the distribution of manganese between molten iron and fused FeO-MnO-SiO_2 slags. Based on these measurements the authors have given an empirical equation for the calculation of the manganese contents of the iron bath when it is in equilibrium with a known FeO-MnO-SiO_2 slag at 1550°C. Considering the slag as constituted of the ions Fe^{++}, Mn^{++}, O^{--} and SiO_4^{4-}, however, and using simple thermodynamics an equation may be derived giving the distribution of manganese between the slag and the metal phase.[8] If the equilibrium constant for the reaction:

$$\underline{Mn} + Fe^{++}_{(slag)} = Mn^{++}_{(slag)} + \underline{Fe}$$

is defined like:

$$K^{Mn} = \frac{a_{Fe} \cdot a_{Mn^{++}}}{a_{Mn} \cdot a_{Fe^{++}}}$$

then K^{Mn} may be calculated from the equation:

$$\log K^{Mn} = \sum_i^n N'_i \log K^{Mn}_i \qquad [1]$$

Here n denotes the number of different kinds of anions, i, in the slag, N_i is the electrical equivalent fraction of the anion i, and K^{Mn}_i is the equilibrium constant for a slag containing only the one kind of anions i. For slags used in the measurements of Bell et al. with only two anions, the equation to be used will therefore be:

$$\log K^{Mn} = N'_{O^{--}} \log K^{Mn}_{O^{--}} + N'_{SiO_4^{4-}} \log K^{Mn}_{SiO_4^{4-}} \qquad [2]$$

and as $N'_{O^{--}} = 1 - N'_{SiO_4^{4-}}$, $\log K^{Mn}$ will be a linear function of $N'_{SiO_4^{4-}}$ (see Fig. 7).

Approximate values of $K^{Mn}_{O^{--}}$ and $K^{Mn}_{SiO_4^{4-}}$ are available from the literature. K^{Mn} for the equilibrium between iron and fairly pure FeO-MnO slags as a function of the temperature is measured by Chipman, Gero and Winkler[4] and by Korber and Oelsen,[5] the average of these two investigations giving:

$$\log K^{Mn}_{O^{--}} = \frac{6350}{T} - 2.99 \qquad [3]$$

This eq 3 is also in good agreement with the measurements by Krings and Schackmann[6] on the distribution of manganese between iron and FeO-MnO-MgO slags within a narrow temperature range (from eq 1 Mg^{++} in the first approximation is indifferent to the distribution of manganese). Eq 3 also fits with the earlier publication.[9]

The manganese equilibrium in silica saturated Fe-

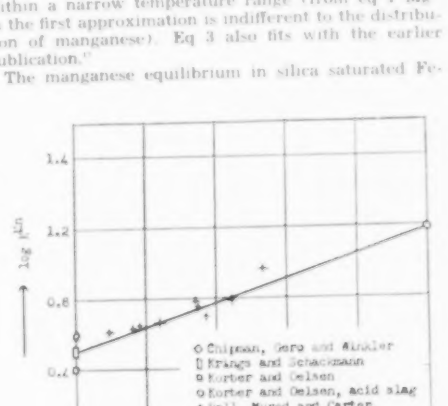

Fig. 7—Dependence of log K^{Mn} on the electrically equivalent ionic fraction of SiO_4^{4-} at 1550°C.

Mn silicates was examined by Korber and Oelsen.[7] They found that

$$\log K^{\%}_{Mn_{(liq)}} = \frac{7940}{T} - 3.172 \qquad [4]$$

Calculations indicate that the manganese distribution shows little dependence on the acidity of the slag as long as the silica contents are beyond the orthosilicate formation. In this composition range one therefore will have $K^{\%}_{Mn_{(liq)}}$ approximately equal to $K^{\%}_{Mn_{(sat)}}$. In Fig. 2 of Bell et al. this also explains the point of inflection of $K^{\%}$ at 20 to 25 wt pct silica, where N_{SiO_2} approximately is like eq 2.

Introducing eqs 3 and 4 into 2 makes it possible to calculate log $K^{\%}$ at different temperatures and by different slag compositions.

If we now introduce concentration terms instead of activities in our equation it will be possible to calculate the manganese content in the iron bath from the slag analysis, if the influence of the activity coefficients is negligible. We thus have:

$$P_{Mn} = \frac{N_{Mn^{++}}}{K^{\%}_{Mn} \cdot N_{O^{--}}}$$

or

$$P_{Mn} = \frac{N_{Mn^{++}}}{N_{O^{--}}} \cdot (K^{\%}_{Mn_{(liq)}})^{N_{SiO_2}} \cdot (K^{\%}_{Mn_{(sat)}})^{N_{MnO}} \qquad [5]$$

Using this equation, where the manganese content is obtained in weight percent, the manganese contents of the iron phase is calculated for the experiments by Bell, Murad, and Carter carried out in a resistance furnace at 1550°C. The calculated manganese contents is given in Table VI together with the results from chemical analysis. The "Heat No." are the same as used by the authors. The agreement between calculated manganese content and analysis is satisfactory except for heat No. 20.

It may be noted that if the equilibrium constant in pure orthosilicates is smaller than the value used from eq 4, $K^{\%}_{Mn_{(liq)}} < K^{\%}_{Mn_{(sat)}}$, then the equilibrium constant of Chipman et al.[8] will make our equation fit better to the measurements of Bell, Murad and Carter than eq 3 does.

Table VI. Calculated Manganese Contents at 1550°C

Heat No.	Mn, Wt Pct	
	Analysis	Calculated
11	0.050	0.053
13	0.04	0.04
14	0.12	0.12
15	0.46	0.48
16	0.40	0.36
17	0.26	0.20
18	0.22	0.22
19	0.032	0.035
20	0.043	0.107

The equilibrium for the silicon distribution between an iron bath and a basic slag may be formulated like:

$$Si + 2O^{=}_{(liq)} = SiO_2^{\%}{}_{(sat)}$$

It is analogous to the phosphor distribution.[9] As far as the author knows, however, there are as yet not sufficient accurate experimental material to check a similar equation for the distribution of silicon.

H. B. Bell, A. B. Murad, and **P. T. Carter**—We are pleased to note the excellent agreement between our results and the calculations of Dr. Grjotheim. Further experiments have confirmed that the K'_{Mn} value for heat No. 20 is high, possibly because of an analytical error in the determination of the small amount of manganese in the metal. We are not clear why manganese distribution should be independent of acidity for slags more acid than orthosilicates. Our experiments suggest that K'_{Mn} for orthosilicate slags is about 10, i.e., considerably less than the value of 15.5 given by Korber and Oelsen for silica-saturated slags. It is probable, however, that the latter figure is too high.

[7] H. Bell, A. B. Murad, and P. T. Carter: Unpublished.
[8] H. Flood and K. Grjotheim: Journal Iron and Steel Inst., 1952, 171, pp. 64-70.

Silicon-Oxygen Equilibrium in Liquid Iron

DISCUSSION, D. E. Babcock presiding

D. C. Hilty (*Union Carbide and Carbon Research Laboratories, Niagara Falls, N. Y.*)—This paper is a very nicely detailed analysis of a difficult problem. I would like to point out that the results that Mr. Crafts and I published a few years ago had no reference to activity, or anything else of a similar nature; our results were strictly empirical. It is quite gratifying that we now have a case where results involving activity coefficients and results derived from direct observations on actual steel melts are practically identical. When two different laboratories, working from two entirely different approaches, come out with results in such good agreement in their major significance, that is an achievement. It is something that was not possible 15 or 20 years ago.

There is one question I would like to ask Dr. Chipman. It has to do with a very minor point of disagreement in these results. When we reported the kink in the Si-O solubility curve I think you may recall that it came at the different temperature levels at about the order of 0.015 to 0.03 pct O and 0.03 to 0.07 pct Si—we also pointed out that we had difficulty in obtaining data at that level, although we finally did get some. I note in going through the data for the present paper, that there are no samples in those particular silicon and oxygen ranges. I wonder if that was purely accidental or was there a reason for it.

D. E. Babcock (*Republic Steel Corp., Youngstown, Ohio*)—Mr. Hilty, do you have any explanation for that discrepancy between Dr. Chipman's curve and your own?

Mr. Hilty—Our explanation for it at that time was that for some reason our system probably was not in true equilibrium with SiO_2, that is, in equilibrium with the silica crucible at that level. We did observe, however, that that was the level at which both the metal and the slag became saturated with SiO_2. On the average, in studying inclusion formation in small ingots permitted to solidify normally from the molten state, we observed pure silica inclusions at silicon contents over about 0.05 pct and FeO type inclusions at silicon

contents below that, and we attached certain important significance to these observations.

John Chipman (authors' reply)—If I understand Mr. Hilty's question, it is: "Why was there no heat in which the silicon content was about 0.05." We did not avoid this range intentionally. It simply happened that no heat fell at exactly this point. No anomaly is expected in this range.

Mr. Babcock—With reference to Fig. 5, a curve could be drawn through the points equally well, if not better, than the straight lines. What is the significance of the two straight lines?

Dr. Chipman—This question emphasizes the danger of a purely statistical interpretation of data. The vertical line at 0.088 oxygen represents heats in which a slag was observed. Such heats should theoretically contain a definite amount of oxygen and in all cases this was observed within ±0.002 pct.

The slanting line was established by Fontana in 1933. Our points fall on this line when the oxygen content is above 0.04 pct, or rather when the silicon is below 0.02 pct. There is only one exception to this in a heat that contained 0.05 pct O at a silicon level that calls for about 0.044. This is regarded as experimental error.

The low oxygen points which are definitely off the line constitute the principal subject matter for this paper. They are out of line because the higher silicon content has diminished the activity coefficient of oxygen.

Mr. Hilty—In support of what Dr. Chipman has said, in oxygen solubility papers by Mr. Crafts and myself some of the results that we did not publish at the time because it seemed superfluous included statistical analysis of our data. We plotted our data up to about 4 pct Si and ran a statistical analysis on them. We found out that the curve above 0.10 pct Si was not a straight line of the slope that would be expected for a simple %Si x (%O)^2 relation. The slope of the line on a logarithmic plot was actually −2.12 instead of −2.0 with a tendency toward deviations from the straight line at both high and low silicon ends and I believe that that is evidence supporting Dr. Chipman's comments relative to the effect of silicon on the activity of oxygen at that level.

Dr. Chipman—Mr. Hilty refers to the line of Fig. 9. Does the question concern the fact that the point at 5 pct Si is a little below this line.

Mr. Hilty—Not necessarily, but you remarked about the fact that while those data are represented by a straight line, there really is no reason for it, according to the effect of the elements on their activities.

Dr. Chipman—It is true that the activity coefficients of silicon and oxygen in some measure offset one another to yield the straight line of this figure. At either end of the line the analytical results are so uncertain, because of the low silicon or oxygen level, that minor departures from the straight line can be ignored.

J. E. Stukel (*Youngstown Sheet and Tube Co., Youngstown, Ohio*)—An extremely important fact has been overlooked in the discussion of this paper, that is, the excellent agreement of the present results with those published by Hilty and Crafts indicates that the presence of hydrogen in this system does not have a significant effect on the equilibrium. If this is proved to be the case in other systems, the technique employed by Chipman and coworkers may be accepted without reservations. As a matter of interest, when manganese is melted in a silica crucible as much as 18 pct Si is found in the metal. This indicates that manganese plays a definite role in the reduction of silica.

Dr. Chipman—In reply to Mr. Stukel's comment, I should like to say that we have independent evidence that hydrogen does not affect the equilibrium under consideration otherwise than expressed in the ratio H_2O/H_2. Dastur's work on the same equilibrium in the absence of silicon resulted in equal values of K when the gas system consisted of four parts of argon per part of hydrogen and when argon was omitted. In view of the very small solubility of hydrogen in the molten metal, this agreement was expected.

C. E. Sims (*Battelle Memorial Institute, Columbus, Ohio*)—The authors make critical mention of the work of Zapffe and Sims. For example, it is suggested that equilibrium was not reached because of insufficient holding time. That earlier work was done under somewhat cruder conditions than the highly refined techniques that have been developed at M.I.T., but short cuts to equilibrium were taken by starting with compositions already close to the equilibrium to be attained. This would require much less time, and it was checked by working on both sides of the equilibrium. This technique apparently was used by the present authors. Scatter in the work of Zapffe and Sims is more likely the result of erratic analyses.

The authors say of Zapffe and Sims, "Their results did indeed indicate that the activity coefficient of oxygen is decreased by the presence of silicon, although they made no such simple statement." It would indeed have been a simple statement to make, but it would explain nothing. What we did show, probably for the first time, was that the concentration product of silicon and oxygen, or K', is not a constant for varying conditions. It could have been corrected by an appropriate factor, conventionally known as an activity coefficient but which might as well have been called an availability coefficient. Such a factor, of course, as the authors show, is not a constant either, but must be adjusted continuously for both concentration and temperature.

There must be some good reason why silicon and oxygen, when both are present in iron, act as though they are not "all there." One suggested reason is that the wrong equation is being used to express the reaction. We were curious and attempted an explanation, for which effort we are now chided. Perhaps the explanation was wrong, but if so, we would like to see a better one. As to the unlikelihood of SiO being involved, suffice it to say here that, at steelmaking temperatures, SiO is just as real as CO.

We could have called this marked deviation from ideality an activity coefficient and have served the ends of thermodynamics. However, thermodynamics is not an end, but rather a means to an end, which is to enhance our basic knowledge. I believe that an understanding of mechanisms will do more to advance our science than an amassing of constants, useful though the latter may be.

Dr. Chipman—The authors share Mr. Sim's scientific curiosity and would greatly welcome an adequate explanation for the large effect of silicon on the activity coefficient of oxygen. We feel, however, that the data are valuable whether or not such an explanation can be obtained. The use of activity coefficients rather than hypothetical formulas simply recognizes the fact that thermodynamic data can be useful without the necessity for inventing molecular models.

G. R. Fitterer (*University of Pittsburgh, Pittsburgh*)—The contributions of Dr. Chipman and his students to the science of physical chemistry of steelmaking have continued to be excellent and important to its development. Their work is usually conducted with such excellent laboratory technique that there is seldom any question regarding the validity of the data as reported. Nevertheless, one is not forced to always agree with their interpretation of data; in fact, Dr. Chipman would be the first to suggest that differences in opinion can only strengthen the science. It is for this reason that the following discussion has been prepared.

The authors were not benevolent in their remarks concerning previous investigations in this field, particularly the work of Dr. Herty and myself.[4] It hardly seems ethical to label our work "crude" when one considers that it was done twenty-six years ago, long before the many research tools which were used by the present authors became available. At that time, there were no high frequency induction furnaces, no vacuum fusion methods, little verified knowledge of thermo-

dynamic equilibria, and in fact, Lewis and Randall's system of thermodynamics which is generally accepted today was only three years old when our work was completed.

Had all of these tools been available, I have no doubt that we would have used them. Nevertheless, lacking all of these tools, a deoxidation constant of $K_c = (\%\ Si)(\%\ O)^2 = 0.62 \times 10^{-3}$ was obtained at 1600°C. This is to be compared with the value of 2.8×10^{-3} which was determined by Gokcen and Chipman in this paper. The latter value also seems to check the excellent work of Hilty and Crafts,[2] as illustrated in Fig. 14 of the paper under discussion.

Because of the fact that I feel that it is due time to get on with the practical application of these constants, I would be only too happy to agree that the constant which has been developed and checked by these two sets of investigators is correct, and that ours was close but not exact. I would agree to that provided that I honestly felt that all factors had been considered by the authors of this paper.

Actually, neither Gokcen and Chipman nor Hilty and Crafts made use of a tool which Herty and I felt was necessary in order to develop the deoxidation constant. This was the extraction and analysis of the nonmetallic inclusions in all samples. Both groups of investigators made a statement in passing that the inclusion content of their samples was "insignificant." Apparently, they did not realize that only an extremely small quantity of SiO_2 particles in a sample will greatly change the value of the deoxidation constant.

Gokcen and Chipman stated (p. 173) that "insoluble silicon was determined by either method and found to be of the order of 0.004 pct." Also, the apparent accuracy of their silicon method varied from ±0.002 to ±0.003 pct. The presence of 0.004 pct Si as SiO_2 greatly affects the value of the deoxidation constant as will soon be shown. This amount of silicon would be associated with $0.004 \times \frac{32}{28} = 0.00457$ pct O or the steel would contain 0.00857 pct SiO_2.

If the SiO_2 inclusions are to be ignored in these samples of Gokcen and Chipman, then the deoxidation constant of $2.8 \times 10^{-3} = (\%\ Si)(\%\ O)^2$ would indicate that with 0.10 pct total silicon (assumed), 0.0167 pct total oxygen would be present. However, the "free" or uncombined silicon present at equilibrium in a sample containing 0.10 pct total silicon and 0.004 pct "combined" silicon would be 0.100 − 0.004 or 0.096 pct. Similarly, the uncombined oxygen would be 0.0167 − 0.00457 or 0.01214 pct. Thus, the deoxidation constant corrected for the presence of 0.004 pct combined silicon or 0.00857 pct SiO_2 would be calculated as:

$$K_c = (\%\ Si)_{free}\ (\%\ O)^2_{free} = (0.096)\ (0.01214)^2$$

or $K_c = 1.4 \times 10^{-3}$. This is exactly one-half the value suggested by the authors.

In criticizing the work by Herty and myself[3] in which a K_c value of 0.62×10^{-3} was reported, it was stated that our "temperature measurement was uncertain." Yet, a correction for the presence of 0.004 pct Si as inclusion material will alter the value of K_c as much as will a temperature difference of 50° or 60°C.

In a steel with a normal amount of silicon of 0.28 pct, the oxygen content at equilibrium (i.e., $K_c = 2.8 \times 10^{-3}$) would be 0.010 pct. Do the authors of this paper suggest that the presence of 0.00457 pct O in SiO_2 inclusions would be insignificant and may be ignored when it is nearly half of all the oxygen present in such a sample? Only about 0.086 pct of combined silicon (SiO_2) is necessary to change Gokcen and Chipman's constant of 2.8×10^{-3} to agree with that of ours, or 0.62×10^{-3}. This is within the realm of possibility, inasmuch as the amount of combined silicon was found to be 0.004 pct and the accuracy of the analysis was ±0.002 pct.

It is to be regretted that the authors did not analyze all samples for SiO_2 or insoluble silicon and correct their values accordingly. If they had, their constant would have approached that determined by Herty and myself.

In their statement (p. 173) as to the method by which the insoluble silicon was determined, it was indicated that "either" method was used. This apparently referred to the "standard gravimetric method" and "a colorimetric method." However, the standard gravimetric method cannot be used for inclusion determination, and this is the reason that in our work we found it necessary to develop an electrolytic extraction method. May I ask if some new or old extraction procedure was used by Gokcen and Chipman? It was not so stated in their paper.

Hilty and Crafts also assumed that the inclusion contents of their specimens were negligible because of the nature of the rotating crucible type furnace. They extracted these inclusions electrolytically and showed some micrographs, but I do not recall that they reported the amount of insoluble silicon and subtracted it from the total to establish their constant. It might be assumed that their insoluble silicon was of the same order of magnitude as that reported by Gokcen and Chipman. If so, one would expect these two investigations to check one another.

All of these thoughts lead one to suggest that the modern trend of writing the reaction between oxygen and silicon in liquid iron as $\underline{Si} + 2\underline{O} = \underline{SiO_2}$, with the underlines indicating that the silicon and oxygen are dissolved in liquid iron, is open to criticism. This is particularly true when one considers that this method of expression has become conventional, as in the AIME "Basic Open Hearth" book. Students who are taught to write the reaction as above may incorrectly assume that it is only necessary to analyze for silicon by the gravimetric method and oxygen by the vacuum fusion method in steels deoxidized with silicon. However, the gravimetric method reports the total silicon (i.e., both the uncombined plus the silicon combined as SiO_2). Also, the vacuum-fusion procedure determines the oxygen in the SiO_2 inclusions as well as that which is dissolved in or associated with the iron.

At the expense of being old-fashioned but with the objective of teaching students to avoid this pitfall, the writer still prefers to write the reaction as:

$$Si_{(dissd.)} + 2FeO_{(dissd.)} = SiO_{2(s)} + 2Fe_{(l)}$$

with the statement that the silicon and "FeO" are dissolved and dissociated in the liquid iron, whereas the SiO_2 is present as small solid nonmetallic inclusions distributed throughout the metal. The metal may actually be in more intimate contact with such inclusions than with the slag or crucible walls. In other words, the equilibrium probably involves the presence of SiO_2 inclusions, and all ordinary steels contain such particles. It is not necessary to consider the SiO_2 of the crucible walls in this heterogeneous equilibrium because SiO_2 particles are suspended throughout the liquid metal.

This latter method of writing the equation suggests that both dissolved (or free) silicon and the silicon combined as SiO_2 must be determined separately. Also, a correction must be made for the oxygen which is combined as SiO_2 to distinguish it from that which is free or unassociated. Otherwise, incorrect analyses of the data and a large error in the calculation of the constant will result.

Probably the samples which were studied by Gokcen and Chipman as well as Hilty and Crafts express the ultimate in experimentally reducing the SiO_2 content to a minimum. Yet, the small amounts of these impurities which were present in their samples were obviously sufficient to change the deoxidation constant from 2.8×10^{-3} to 1.4×10^{-3} or less. The fact that the oxygen value is squared in the constant is responsible for this marked difference.

Chipman reported that as much as 20 hr were neces-

sary to establish equilibrium in some samples. Could it be that the minute insoluble SiO_2 particles were slowly rising out of the bath during this period? Because of the heterogeneous nature of this reaction, equilibrium might have been established in a few seconds and the true equilibrium constant is not dependent upon the quantity of insoluble SiO_2 particles suspended in the liquid—only their presence is required. However, analysis of the steel for total silicon and total oxygen would indicate a very slowly changing analysis due to the elimination of inclusions. But the "free" silicon and "free" oxygen might have attained equilibrium within a very few seconds with any quantity of precipitated SiO_2 particles which may have been present. The activity of SiO_2 in the constant would be unity with one or with a million particles.

The writer would suggest a return to the older method of writing the reaction so as not to give a false impression to the uninitiated as to the importance of analyzing the samples for SiO_2 inclusions. In all practical steels which have been deoxidized with silicon, the SiO_2 content is much larger than in the samples discussed herein, and thus mathematically more important in the practical application of the deoxidation constant through the determination of free silicon and oxygen. Gokcen and Chipman as well as Hilty and Crafts have used the total silicon and total oxygen for their calculation. Only the "free" or unassociated values should be used in the calculation of a deoxidation constant. It is to be regretted that the analyses for inclusion material were omitted in these experiments because the work was excellent in every other detail. The exact value for the deoxidation constant is not yet established.

Dr. Chipman—It is regretted that Professor Fitterer interpreted our remarks in a personal light. The authors, in keeping with all other metallurgists cognizant of the early work of Herty and his colleagues, recognize the very valuable contribution that Dr. Fitterer and others made to our early understanding of the physical chemistry of steelmaking. We doubt that many people would disagree with us in considering the experimental techniques of the 1920's as "crude" when viewed by modern standards.

The principal difference in interpretation of our results seems to hinge on the insoluble silica present in the specimens. We have assumed, along with Hilty and Crafts and many others, that the nonmetallic inclusions present in such samples are formed during solidification rather than at the melting temperature. This assumption is based on the pioneer work of Sims and Lilleqvist[1] which has been confirmed so many times. Our data on rate of approach to equilibrium cannot be used to support the idea that "minute insoluble SiO_2 particles were slowly rising out of the bath." Reference to Table IV shows that in heats beginning with pure iron, the product [% Si] × [O]^2 remains substantially constant over a period of 16½ hr. If inclusions were present in the metal and were gradually floating out, it is difficult to see how such a constancy could be maintained. Even in the heats in which a high silicon charge was used, the product, when corrected by activity coefficients, is again substantially constant. Moreover, the authors have shown very clearly that the slow approach to equilibrium was associated with the slow transfer between gas and metal rather than to any phenomenon within the metallic phase.

All of our calculations then are based on the assumption that the total oxygen and total silicon in the solidified ingot represent the composition of the liquid metal. If this assumption is wrong, then not only our work but also that of Hilty and Crafts and of Körber and Oelsen must be discarded. From this viewpoint it does not matter what fraction of the total silicon and oxygen content of the ingot remains undissolved when the sample is treated with acid, so long as the analysis yields the total amount of each element. We would expect that this residual might be more nearly related to the rate of freezing rather than to any other variable.

J. Pearson and **E. T. Turkdogan** (*British Iron & Steel Research Association, London, England*)—The authors are to be congratulated on a piece of fine experimental work, the results of which cannot fail to be of great use to those studying the physical chemistry of steelmaking processes. No doubt they will take their place among that series of data from Professor Chipman's school to which all process metallurgists constantly refer.

It is known that the activity coefficient of oxygen remains constant in a binary Fe-O system up to saturation, i.e., $\partial \ln \gamma_O / \partial x_O = 0$, from which it follows from the Wagner equation that $\partial \ln \gamma_{Si} / \partial x_O = \partial \ln \gamma_{Si} / \partial x_{Si} = 0$. This is patently at variance with the results in Table VII and Fig. 6, and is further evidence that Wagner's equation is not valid for the Fe-Si-O system.

Referring to the results shown in Fig. 6, it should be noted that these have only limited value. They certainly do show the effect of a given percentage of silicon on the activity coefficient of oxygen but at only that concentration of oxygen, given for the appropriate silicon content in Table VII, which is in equilibrium with that silicon content and solid silica. It will require further work to ascertain how the value of $\log f_O^{(Si)}$ for, e.g., [Si] = 0.1 pct varies from −0.1 at 1600 C for oxygen contents lower than the value which is in equilibrium with 0.1 pct [Si] and solid silica, such as will occur when the silica is dissolved in a slag. It is with such $f_O^{(Si)}$ values that the steelmaker will be concerned.

Dr. Chipman—The application of Wagner's equation requires some further explanation in view of the remarks of Drs. Pearson and Turkdogan. Our eq 6 is the same as Wagner's eq 15 and is strictly valid in any ternary system in which the concentrations of components 2 and 3 approach zero. The extension of this equation applied by Professor Wagner in his study of amalgams is not expected to fit the present case. It was specifically stated in Wagner's paper that his eq 16 is significant only if the deviation from ideal behavior for the two binary systems have equal signs. Further it should be noted that his entire discussion was restricted to metallic solutes and the derived equations are not expected to be applicable to a solute such as oxygen.

Eq 6 is then valid in the present case at infinite dilution and the value of the coefficient is not zero. The next question raised by Drs. Pearson and Turkdogan is to what extent is this coefficient independent of composition. Obviously there are difficulties enough attached to the study of the system Fe-Si-O and the data are quite inadequate to answer this question. It has been tacitly assumed that the value of $\partial \log f_O / \partial$ [% Si] is independent of the oxygen concentration. This assumption appears to be well justified by the extreme dilution of the solution and by experience with other systems. It has been shown,[2] for example, on the basis of data of Körber and Oelsen that the value of the corresponding coefficients for the effects of phosphorus, carbon, and nickel on the activity coefficient of silicon are independent of the manganese and silicon concentrations over a wide range of compositions. Further it has been found recently by Sherman and Chipman[3] that the effect of manganese on the activity coefficient of sulphur is independent of the concentration of sulphur up to concentrations higher than 1 pct S.

For a more complete discussion of the relations between solutes in ternary solutions, the reader is referred to Professor Wagner's new book.[4]

[2] See the more complete discussion of this point by Chipman: *Metal Progress* (August 1949) p. 211.
[1] Sims and Lilleqvist: *Trans.* AIME (1932) 100, p. 154.
[3] Chipman: Discussions of the Faraday Soc. (1948) No. 4, p. 46.
[3] Sherman and Chipman: Journal of Metals (June 1952); *Trans.* AIME, p. 597.
[4] Wagner: *Thermodynamics of Alloys* (1952), pp. 51-52. Addison-Wesley Press.

Discussion — Extractive Metallurgy Division*

New York Meeting, February 1952 and Mexico City Meeting, October 1951

Relationships Between Germanium and Cadmium in the Electrolysis of Zinc Sulphate Solutions (paper by S. T. Ross and J. L. Bray. JOURNAL OF METALS, June 1951, p. 465) 1178

Volatility and Stability of Metallic Sulphides (paper by C. M. Hsiao and A. W. Schlechten. JOURNAL OF METALS, January 1952, p. 65) 1179

Mechanism of the Reduction of Oxides and Sulphides to Metals (paper by C. Wagner. JOURNAL OF METALS, February 1952, p. 214) 1179

Observations on the Preparation of Iodide Titanium (paper by O. J. C. Runnalls and L. M. Pidgeon. JOURNAL OF METALS, August 1952, p. 843) 1180

Minerals Beneficiation Division, Mexico City Meeting

Deleading Zinc Concentrate at the Parral and Santa Barbara Mills (paper by C. L. Boeke and G. G. Gunther. JOURNAL OF METALS, July 1952, p. 729) 1181

* TP 3392D

Relationships Between Germanium and Cadmium in the Electrolysis Of Zinc Sulphate Solutions

by S. T. Ross and J. L. Bray

DISCUSSION, R. A. Young and L. P. Davidson presiding

E. M. Ritchett (*Johnstown, Pa.*)—The fact stated by the authors that "In the laboratory, without marked efficiency decreases, the authors have deposited zinc successfully from solutions containing as high as 1 g per liter of germanium," (p. 465, paragraph 3) is most unusual. A similar statement is made in the summary and conclusions: "Germanium alone, within normal operating limits does not cause large efficiency losses." The limits are not defined. These facts are directly contrary to much of the published history on the effect of germanium in zinc electrolysis. A description of the conditions leading to such a successful electrolysis would be of interest to all engaged in the production of electrolytic zinc.

It is unfortunate that the authors of this paper did not determine the actual concentration of germanium and cadmium in the solutions which they electrolyzed after a zinc dust purification. This purification will take out a variable amount of these impurities, depending upon the composition of the dust, type of agitation, presence of activating agents, etc. Probably every electrolytic zinc plant in this country has accurate methods, both wet and spectrographic, for determining germanium and cadmium. These specific methods, adopted from the standard analytical literature, are often available to educational institutions for the asking.

The headings of Fig. 2 and of the two tables, with their definite concentrations of germanium and cadmium (which are not so definite according to the footnotes) could possibly be somewhat misleading, since the actual amounts of germanium and cadmium present during electrolysis are not known.

Even the 1 hr electrolysis time might be too short for a study of this type; 12 or 24 hr tests might be much better. Commercial solutions have been known that gave over 90 pct ampere efficiency during the first hour of electrolysis, but no metal at all after 24 hr.

Volatility and Stability of Metallic Sulphides

by C. M. Hoke and A. W. Schlechten

DISCUSSION, H. H. Kellogg and A. J. Phillips presiding

O. W. Moles (*National Lead Co., Sayreville, N. J.*)—The use of the equation $W = P\sqrt{\frac{M}{2RT}}$ to determine vapor pressures is probably not valid under the conditions of the experiments here described. W represents the weight of gas molecules crossing a plane in one direction under equilibrium conditions and applies to the plane at the surface of the solid or liquid as well as to any other plane. Most of the molecules crossing the plane at the surface from the condensed phase to the gas phase have just evaporated. Possibly 10 pct have been reflected from the condensed surface. If it is possible to capture all the molecules which have evaporated from the surface plane, a like number (plus the number normally reflected) would cross any other plane (in one direction) in the equilibrium gas and therefore the above equation could be used to calculate the equilibrium gas pressure. However, under the conditions of the experiments it appears probable that a large proportion (90 pct or more) of the molecules which evaporated recondensed on the solid or liquid face. The residual gas pressure (10^{-4} mm) is relatively high compared to the measured pressures (10^{-3} to 10^{-1} mm) and considerable surface is available for molecules to reflect from. The results of Veselovskii and Pogorelyi which are twenty to forty times greater than those given by this investigation for ZnS may be more nearly correct.

It might be suggested that the data may be better treated as a problem of diffusion, but this is not very hopeful because of the lack of diffusion coefficients and other necessary information.

Vapor pressures of substances such as sulphides are important and it is hoped that the present authors and others will continue work on the problem and finally determine the desired information.

E. J. Kohlmeyer (*Berlin, Germany*)—I would like to call your attention to two earlier publications[a] on the boiling points of metallic sulphides. The determinations were made at atmospheric pressure by heating the sulphides up to boiling and by controlling the temperature with a dipping Pt-Pt-Rh thermocouple. The boiling of the sulphides PbS, Sb_2S_3, and SnS is accompanied by a simultaneous dissociation. This is the reason why the boiling point is continuously rising, because of the enrichment of metal in the sulphide melt. In such manner antimony sulphide is completely dissociated and the boiling point rises from 885°C, the boiling point of Sb_2S_3, to 1635°C, the boiling point of Sb.

Since the sulphides PbS and SnS are only partially dissociated, the boiling continues. The melting and boiling points of ZnS are close together, 1620° and 1650°C.

In the presence of carbon the boiling points of all sulphides are lowered because of the formation of unstable compounds of the type *MeCS* existing only in the form of vapor.

N. A. Gokcen (*Michigan College of Mining and Technology, Houghton, Mich.*)—The slopes of the straight lines in Fig. 2 for liquid and solid As_2S_3 are defined by the following relation:

$$\text{Slope} = \frac{d \log P}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H}{4.576}$$

where ΔH is either the heat of sublimation or vaporization. This equation is also valid when the indirect pressure measurements differ from the true pressure values by a constant factor.

Since $\Delta H_{\text{sublimation}} > \Delta H_{\text{vaporization}}$, then the slope of the sublimation line must be smaller than that of the vaporization line. The slopes in Fig. 2 are thus in disagreement with these thermodynamic considerations.

A. W. Schlechten (authors' reply)—We are inclined to agree with Dr. Moles that the uncertainties of the experimental method make it advisable to consider the results as apparent vapor pressures, as we labeled them. However, we were encouraged to find that our method when used on copper checked very well with the determinations of other workers, and these were for pressures also much lower than the residual gas pressures.

The interesting experiments of Dr. Kohlmeyer emphasize the fact that at high temperatures dissociation becomes the dominant mechanism of weight loss for certain sulphides.

The variance of our data pointed out by Dr. Gokcen may be the result of decomposition of As_2S_3 to As_2S_2, as noted on p. 68 of the paper, to a greater extent above the melting point. The latter compound has the higher vapor pressure.

[a] *Metall u. Erz* (1932) 29, pp. 105-113 (1939) 36, pp. 578-584

Mechanism of the Reduction of Oxides and Sulphides to Metals

by Carl Wagner

DISCUSSION, H. H. Kellogg and A. J. Phillips presiding

J. Pearson (*British Iron and Steel Research Association, London, England*)—Dr. Wagner has referred to the work of Richardson and Dancy and Gellner and Richardson on the reduction at 900°C of wüstite films on iron. He has assumed that iron ions and electrons migrate backwards to the iron-wüstite interface and that the reduced iron grows on the metal substrate. This would be a possible explanation of the results of these workers were it not for the fact that, as stated by Gellner and Richardson but not stressed, this growth in the center of the specimen can occur even

if the whole cross section has been oxidized, provided that the oxidation treatment is terminated shortly after the metal has been oxidized throughout.

It was at my suggestion that the late O. H. Gellner carried out such an experiment and I studied the cross sections of these completely oxidized and partially reduced samples with care. Their appearance was the same as those which had been only partially oxidized before reduction, except that there was none of the original substrate left. It must therefore be assumed that iron atoms or iron ions and electrons migrated toward the recently formed wüstite and nucleated there. Gellner and Richardson made suggestions as to why nucleation should be easier in the recently formed wüstite than in that at the outer surface of the samples.

It appears that the iron substrate is necessary only to produce the condition, be it due to strain or other causes, which favors easy nucleation, since its effect persists even when the iron has been all oxidized. When a fully oxidized specimen is annealed and then treated with hydrogen, reduced metal does not build up preferentially in the center of the strip but each recrystallized grain is reduced from its boundaries inward.

All specimens reduced at 700°C showed reduction at and from the outer surface only. This is presumably because diffusion of iron atoms or ions is then so slow that the critical nucleation concentration can be exceeded in the outer layers before the requisite but lower concentration is reached in the layers in contact with the iron or just formed from it.

It is, therefore, to be concluded that Wagner's overall picture of the mechanism is correct but that combination of metallic ions and electrons and nucleation may be dependent on some physical property of the oxide.

Carl Wagner (author's reply)—The author is grateful to Dr. Pearson for his remarks. Further research on the reduction of wüstite seems very desirable. In particular, reduction of wüstite should be investigated in an atmosphere of water vapor and hydrogen rather than in pure hydrogen. The formation of fresh nuclei will be more probable in pure hydrogen (containing water vapor only as far as formed by the reduction of oxide) than in an atmosphere of hydrogen with a definite amount of water vapor. If the H_2O/H_2 ratio is just slightly lower than equilibrium ratio for coexistence of iron and wüstite, growth of retained iron particles rather than fresh nucleation is expected. Experiments in a H_2-H_2O atmosphere may therefore lead to more conclusive results and may especially make possible a more distinct differentiation between the reduction of freshly formed wüstite and the reduction of aged wüstite.

Observations on the Preparation of Iodide Titanium

by D. J. G. Ives and J. M. Pearson

DISCUSSION, N. Arbiter and O. C. Ralston presiding

J. M. Blocher, Jr. and **I. E. Campbell** (*Battelle Memorial Institute, Columbus, Ohio*)—Since the de Boer-Van Arkel process for making titanium metal involves a number of steps in a fairly compact unit, it is difficult to determine simply which of the steps is rate controlling. In any statement as to which step constitutes the rate-controlling process, qualifications appear to be in order.

It is possible to design a reaction bulb in which any one of a number of steps is made to be controlling. 1—With the filament removed some distance from the crude, as in the case of the authors' experiments, the interdiffusion of iodine and iodide may be controlling. 2—If, as is usually done, the crude metal is placed in a perforated cylindrical basket, or as a briquetted mass, in close proximity to the filament, the rate of deposition is increased (we obtained rates of deposition 5 to 10 times those cited in the authors' paper), and another rate-limiting factor, such as the reactivity of the crude, may take over. In this regard, we have noticed radically different rates of deposition with different crudes, and with crudes in various stages of exhaustion. 3—With a very reactive crude metal and with optimum practical geometry, still another process may be controlling. It is felt that this is a diffusion process in the immediate vicinity of the filament involving the fundamentally adverse situation of a net flow of particles away from the filament.

The separate experiments on the reactivity of iodine with titanium are interesting but somewhat inconclusive. Data is still needed on the partial pressure of iodine in an operating decomposition bulb. A knowledge of the gradient of iodine partial pressure from the crude to the filament would be particularly enlightening. Optical absorption may be a useful technique here. Accurate measurements of the total pressure within a decomposition bulb under various conditions would be quite revealing. Preliminary measurements have been made at Battelle in following this line of attack.

It is interesting to note that the authors' data on the temperature dependence of deposition rate indicate that the overall rate is not controlled by the kinetics of the decomposition reaction at the filament:

$$TiI_4 \rightarrow Ti + 4I$$

Any reasonable estimate of the activation energy of this reaction would, if its kinetics were controlling, dictate a much greater temperature dependence than is observed here.

The authors apparently attribute the drop in deposition rate (eventually to zero) with increased TiI_4 pressure solely to a decrease in diffusion rate. However, there is an equilibrium factor involved here that must not be overlooked. As the partial pressure of TiI_4 is increased, a point is reached where, due to the competing reaction of the tetraiodide with titanium to form lower iodides, the equilibrium partial pressure of titanium is reduced to the point that it equals the vapor pressure of titanium at the filament temperature and the deposition rate falls to zero. This effect would

be observed even though the rate of removal of iodine from the deposition zone were not a function of pressure. If this limiting pressure of TiI$_4$ is exceeded, titanium is actually removed from the filament. This effect cannot be explained solely on the basis of TiI$_4$ acting as a barrier to the diffusion of iodine.

Incidentally, the use of mg per sq cm per hr as a measure of the rate of deposition is somewhat misleading as it implies that the rate of deposition is proportional to the diameter of the filament, which is not the case. In depositing titanium at Battelle on filaments varying over a 1 to 100 range in diameter, little more than a 1 to 2 variation in deposition rate has been observed under otherwise comparable conditions. This in itself is evidence that the rate-controlling process takes place at some distance from the surface of the filament. A rate expression in terms of weight per unit of filament length per unit of time is more useful.

In conclusion, it should be stated that, from a practical standpoint, the rate at which TiI$_4$ is formed at the surface of the crude is usually the overall rate-controlling factor in the iodide decomposition process for the production of titanium. Under otherwise comparable conditions, forty-fold variations in deposition rates have been observed at Battelle using crude metal charges having different histories. The reactivity of the crude metal is markedly influenced by the presence of oxide or nitride films on the surface, or by the presence of impurities which become concentrated as the titanium is consumed.

Although the reactivity of the crude may be rate controlling under certain conditions, it is recognized that when a highly reactive crude is used, a process other than the synthesis step may become controlling. However, it is felt that this occurs at rates of deposition substantially in excess of those reported in the paper.

O. J. C. Runnalls and **L. M. Pidgeon** (authors' reply)—The observations of Blocher and Campbell on the practical large-scale deposition of iodide titanium are interesting and, presumably, represent an extension of the last published work[1] on the subject.

For the reaction:

$$TiI_4 \rightarrow Ti + 4I$$

if a reasonable estimate of the activation energy is assumed, about 30 kcal, and for an accommodation coefficient of unity, the measured temperature dependence of deposition rate was what might have been expected up to 1400°C. Above this temperature, it is reasonable to assume that the volatility of titanium would result in a lower deposition rate than expected if the kinetics of this process alone were controlling the deposition.

One could speculate further concerning the decrease in deposition rate with increase in TiI$_4$ pressure above 15 mm Hg and attribute this phenomenon, at least in part, to the increased effect of thermal diffusion in the region of the hot filament at higher pressures of TiI$_4$.

Blocher and Campbell's use of the term rate of deposition is somewhat confusing. Apparently they are referring to the total weight of titanium deposited per unit of time. In the work described, the authors found that the deposition rate was independent of the filament area exposed. Hence, the use of the term mg per sq cm per hr was considered legitimate in describing the deposition rate.

Deleading Zinc Concentrate at the Parral and Santa Barbara Mills

(Any discussion resulting from presentation at the Los Angeles Extractive Metallurgy Division Meeting will appear in the November 1953 issue.)

I. M. Symonds (*Cia Minera de Penoles, Monterrey, N. L., Mexico*)—This is a most interesting paper describing zinc deleading operations. Mr. Gunther was kind enough to show me his operation last fall. Outside of the excellent results, I was most impressed by the ease of control. I had expected a difficult operation requiring careful control and supervision, but found one requiring little attention.

The only disappointing fact of the separation is the poor copper recovery in the concentrate of the deleading float. The final zinc concentrate still has about 3 pct chalcopyrite (assuming the copper is chalcopyrite) which adversely affects the zinc grade. If the copper mineral is free, the poor recovery is probably due to the high cyanide concentration. Fortunately, about 75 pct of the copper is recovered before the pulp goes to the zinc circuit.

Mr. Gunther's remarks about proper cyanide to zinc sulphate ratios cannot be overemphasized. Although our experience has been mostly confined to the conventional Pb-Zn separation, we have found these ratios most important, and more important in the mill than in the laboratory. The laboratory appears to give optimum results over a wider range of reagent control than the mill, especially in regard to the effect of cyanide.

In the mill in handling relatively high grade ores, we usually find that ratios of cyanide to zinc sulphate of 1 to 10 or 20 or higher work best. Where there is a substantial amount of chalcopyrite present, it has been noted that cyanide in the range of 0.02 to 0.10 lb per ton of ore is often beneficial in zinc rejection and possibly in copper recovery in the lead concentrate, while larger amounts, say 0.20 to 0.25 lb per ton, will float more zinc and cause a serious rejection of chalcopyrite. On an ore with 15 to 20 pct Zn content, we have had to use 0.8 to 1.2 lb of zinc sulphate per ton of ore with the above cyanide to obtain optimum results.

Sometime ago we made a laboratory study following Parral and Santa Barbara practice on an ore which never had a very satisfactory rejection of zinc in the lead concentrate. The results were not encouraging and a mill test was not run. Since then the study has been reopened using fresh zinc concentrate from the mill in the laboratory instead of one made in the laboratory. A reasonably clean lead float from the zinc concentrate was obtained. It has been checked several times and each time the zinc concentrate made in the mill responds and the one made in the laboratory does not. Although undoubtedly some reasonable explanations can be given, it is presented here only

as an interesting observation that may be of use to others.

I. H. Lange (*The Gallagher Co., Salt Lake City, Utah*)—I would like to add to this an experience of mine along the same lines except a little more exaggerated on a property in Southwest Africa treating dumps which were very rich in copper, lead, and zinc. On a certain fraction of these dumps, some 200,000 tons, averaging about 4 pct Cu, 6 pct Zn, and 10 to 12 pct Pb, selective flotation was practically out of the question. A technique was developed for the treatment of these ores in which a bulk float of the sulphides was made, the cleaned bulk concentrate being then treated with dichromate and American Cyanamid reagent 610 for the depression of the lead and copper sulphides. Dichromate alone had but little effect, but the combination of this reagent and 610 produced quite a satisfactory result. In the early work, selective flotation of some of the easier floating sulphides of lead and copper was attempted but without much success. However, on some of the upper level mine ores, this scheme is now being used before the bulk flotation of the more difficultly floating sulphides of copper, lead, and the easy floating zinc. Sufficient soluble copper is present in these dump ores that no copper sulphate was needed to activate the zinc, the bulk flotation being carried out with soda ash, xanthate, and frother. This procedure does not make as high a grade zinc concentrate as is made at Santa Barbara, but the company had a very good contract for their zinc concentrates in Belgium getting pay for the copper and lead in the concentrates. Consequently, this treatment paid off on these difficult oxidized sulphide ores.

Norman Weiss (*American Smelting and Refining Co., Salt Lake City*)—Since I was in the Santa Barbara area for a long time, I am somewhat familiar with the deleading operations in that district. At Santa Barbara we started deleading in 1941 and 1942 when we ran into some oxidized ore from the Coyote mine. We found it difficult to float all of the lead without floating zinc also. At that time the zinc concentrate ran about 53.5 pct Zn and 3 pct Pb. This product was not acceptable at the zinc smelter because of its high lead content. Consequently, after some experimentation we put in a deleading section.

The zinc concentrate was first conditioned with cyanide and zinc sulphate, also a small amount of soda ash. Sodium bicarbonate and sodium hydroxide were also used as the alkaline reagent. After the concentrate had been conditioned a lead froth was made, and the resulting tailing (zinc concentrate) ran only 1.8 to 2 pct Pb, which was satisfactory.

Very many Pb-Zn mills now successfully separate lead from the zinc concentrate in some way or another, particularly in the northwest. Some take a zinc flotation middling and refloat this for lead; others have filtered and dried the zinc concentrate before deleading.

However, the contribution that Messrs. Gunther and Boeke have made to this art is very important for the reason that for the first time they have deliberately permitted lead to escape from the lead circuit in order to improve selection there, and then have gone ahead to pick it up out of the zinc concentrate. As far as I know, this is the first time that this has been done.

This seems to be a valuable technique for Pb-Zn ores containing copper. On the normal Pb-Zn ore containing very little or no copper, the zinc content of the lead concentrate may be held below 3 or 4 pct without much difficulty. When the ore also contains copper the problem is more difficult, and the operator has the choice of accepting a lead concentrate containing 7 or 8 pct Zn or even more, or else of upgrading the lead concentrate and sacrificing precious metals and copper. The method used in the Parral district and described by the authors, therefore, may be successfully used on other ores of this type.

H. S. Wildman (*American Smelting and Refining Co., Arales, Chih., Mexico*)—At the present time at the Santa Eulalia mill we are treating the leasers' ore from the Santa Barbara district and as these ores are obtained at or near the surface they contain a great deal of the semioxidized or slow floating lead which tends to report in the zinc concentrate.

As we have not as yet been able to install a zinc concentrate deleading unit such as they are using at the Santa Barbara mill, we have resorted to the tabling of the lead tails prior to zinc flotation. A fair portion of this so-called slow floating lead has been recovered and at the same time the lead float has been stabilized. The previous tendency had been to add a surplus of collector agent to prevent so much lead passing over to the zinc float and at times lowering the grade below the shipping requirements.

C. F. Zeuch (*The Dow Chemical Co., Pittsburg, Calif.*)—In all this work, has anything been done in heating the zinc concentrate before attempting to delead it?

G. G. Gunther (authors' reply)—No work has been done at Parral or Santa Barbara to investigate the effect and the possible use of heat in the zinc deleading operations, mainly because a cheap source of heat is not available at either plant.

E. H. Crabtree, Jr. (*Eagle Picher Co., Miami, Okla.*)—First, I might answer Mr. Zeuch's question on the effect of heat on differential separation. We have one operation now which is being conducted on an old slime pond. This slime pond resulted from muddy primary thickener overflows, which had accumulated for many years because the thickeners were too small for the tonnage being handled. A few years ago we attempted to clean out this slime pond and re-treat it. It contained several percentages of combined lead and zinc. Since we were unable to make a satisfactory selective separation by conventional means, which we assumed was due to the extremely fine sizes, we finally made a bulk Pb-Zn concentrate which is cleaned and filtered and then conditioned in what we call our hot conditioner. This bulk Pb-Zn concentrate is given a retention time at boiling temperature for approximately 1 hr with high concentration of sodium metasilicate. After this conditioning period, the material is passed through a hydroseparator for removal of the excess sodium silicate and the high caustic solution which we have there. The underflow from this hydroseparator then goes into a Pb-Zn differential circuit and a reasonably good separation is made. By that I mean that a concentrate of about 65 pct Pb and one of about 58 pct Zn is made. This is, I think, a solution of a particular problem. We have attempted this hot conditioning with sodium silicate on other ores and it was not successful, but it is particularly successful on very slimey material, which, incidentally, has quite a bit of organic material in it which resulted from the original ore.

There is another comment I wanted to make on Mr. Gunther's paper. As we all know, the main virtue of zinc deleading is that we do not have to control our lead circuit so closely, as Mr. Weiss pointed out. We can work more for lead grade and allow some of the lead to go into the zinc concentrate because of the opportunity to recover it later. In all of the Pb-Zn operations which I have had experience with, I have found that once the lead goes through into the zinc circuit, which is usually a high lime circuit, the lead becomes very sluggish and floats slowly. As a result, a large portion of the lead floating in the zinc rougher circuit floats down toward the tail cells. At one of our operations in Arizona we have taken advantage of this. We pull off a zinc rougher concentrate which goes to the zinc cleaners and then to filtration, but the zinc scavenger concentrate which has the large portion of the lead in it is reground in cyanide and then returned to the head of the lead circuit. I think that one virtue of this is that we can grind in quite a high cyanide strength without being afraid of depressing chalcopyrite since any chalcopyrite that is depressed along with the zinc can be recovered in the lead rougher circuit.

Discussion — Institute of Metals Division*

New York Meeting, February 1952

Low Melting Gallium Alloys (paper by R. M. Evans and R. I. Jaffee. JOURNAL OF METALS, February 1952, p. 153) 1184

Solidification Mechanism of Steel Ingots (paper by H. F. Bishop, F. A. Brandt, and W. S. Pellini. JOURNAL OF METALS, January 1952, p. 44) 1184

Model for Dendrite Growth Form in Metals and Alloys (paper by R. B. Pond and S. W. Kessler. JOURNAL OF METALS, December 1951, p. 1156) 1186

Origin of Porosity in Castings of Magnesium-Aluminum and Other Alloys (paper by E. J. Whittenberger and F. N. Rhines. JOURNAL OF METALS, April 1952, p. 409) 1189

Mechanism of Grain Refinement in Aluminum Alloys (paper by F. A. Crossley and L. F. Mondolfo. JOURNAL OF METALS, December 1951, p. 1143) 1190

On the Mechanism of Precipitation in Copper-Beryllium Alloys (paper by A. H. Geisler, J. H. Mallery and F. E. Steigert. JOURNAL OF METALS, March 1952, p. 307) 1196

Metallurgical Mechanism for Mercury Stress Cracking of Copper Alloys (paper by W. D. Robertson. JOURNAL OF METALS, December 1951, p. 1190) 1196

Preferred Orientation in Zirconium (paper by R. K. McGeary and B. Lustman. JOURNAL OF METALS, November 1951, p. 994) 1196

Preferred Orientation of Arc-Cast Molybdenum Sheet (paper by M. Semchyshen and G. A. Timmons. JOURNAL OF METALS, March 1952, p. 279) 1197

Plasticity of Molybdenum Single Crystals (paper by N. K. Chen and R. Maddin. JOURNAL OF METALS, October 1951, p. 937) 1198

Plastic Deformation of Magnesium Single Crystals (paper by E. C. Burke and W. R. Hibbard, Jr. JOURNAL OF METALS, March 1952, p. 295) 1200

Delay Time for the Initiation of Slip in Metal Single Crystals (paper by I. R. Kramer and R. Maddin. JOURNAL OF METALS, February 1952, p. 197) 1200

Diffraction Patterns and Crystal Structure of Si_3N_4 and Ge_3N_4 (paper by W. C. Leslie, K. G. Carroll, and R. M. Fisher. JOURNAL OF METALS, February 1952, p. 204) 1201

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Isothermal Martensite Formation in an Iron-Chromium-Nickel Alloy (paper by S. A. Kulin and G. R. Speich. JOURNAL OF METALS, March 1952, p. 258) 1204

Isothermal Transformation Characteristics of an Iron-Chromium Alloy of Titanium (paper by C. W. Phillips and D. N. Frey. JOURNAL OF METALS, April 1952, p. 381) 1205

Work Hardening-Reannealing Cycle of Pure Silver (paper by M. Balicki and G. Leeds. JOURNAL OF METALS, November 1951, p. 981) 1206

Kinetics and Orientation Relationships of Secondary Recrystallization in Silver (paper by F. D. Rosi, B. H. Alexander, and C. A. Dube. JOURNAL OF METALS, February 1952, p. 189) 1206

Dislocation Collision and the Yield Point of Iron (paper by A. N. Holden. JOURNAL OF METALS, February 1952, p. 182) 1207

Effect of Prior Strain at Low Temperatures on the Properties of Some Close-Packed Metals at Room Temperature (paper by W. C. Ellis and E. S. Greiner. JOURNAL OF METALS, June 1952, p. 648) 1208

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Constitution and Properties of Some Iron-Bearing Cupro-Nickels (paper by E. W. Palmer and F. H. Wilson. JOURNAL OF METALS, January 1952, p. 55) 1216

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Effect of Temperature on the Lattice Parameters of Magnesium Alloys (paper by R. S. Busk. JOURNAL OF METALS, February 1952, p. 207) 1223

Correlation Between Electrical Conductivity and Temperature Coefficient of Resistance of Solid-Solution Alloys (paper by M. Hansen, W. R. Johnson, and J. M. Parks. JOURNAL OF METALS, December 1951, p. 1184) 1225

Internal Friction Measurements on Iron Wires of Commercial Purity (paper by A. Josefsson and E. Kula. JOURNAL OF METALS, February 1952, p. 161) 1228

* TP 3393E.

Low Melting Gallium Alloys

DISCUSSION, T. E. Leontis presiding

J. P. Denny (*General Electric Co., Lynn, Mass.*)—The authors are to be complimented on their comprehensive investigation. The adaptation of the Rosenhain furnace to low temperatures, as described in their Technical Note,[1] is very noteworthy. A complete description of experimental details is not possible in this type of article. However, for the benefit of future investigators of gallium-base systems, it is highly desirable that certain observations relative to their thermal analyses be presented.

A completed Ga-In-Sn investigation suggests that cooling curves on the gallium side of the authors' Ga-Sn-Zn ternary eutectic would not give reliable liquidus points, because of supercooling. Further, the authors' experimental procedures would presumably not lead to extensive supercooling of the entire eutectic, but only to supercooling of the gallium-rich phase of the eutectic. Clarification and/or confirmation is requested.

The authors' experience with systems of immiscible liquids brings to mind what was a rather perplexing problem relative to the Ga-In binary, and a brief description will perhaps be of interest. Preliminary Ga-In melting curves, at high gallium compositions, revealed three transition points, one corresponding to the liquidus, one to the solidus, and one of unknown origin. A second problem soon presented itself: The liquidus could not be found at any composition between 29 and 35 pct In. These two observations suggested that the binary must contain a central region of liquid immiscibility, and chemical analysis procedures were worked out to test this thesis. An alloy of critical composition was prepared, centrifuged, quenched, and top and bottom portions sectioned for chemical analysis. No immiscibility could be detected.

This dilemma was ultimately resolved by: 1—detection of 0.1 pct Hg impurity in a lot of so-called high purity gallium, which was proved to cause the additional transition at 18.2°C, and 2—the use of sensitive cooling curve methods on the indium side of the eutectic. There is a moral here: if all gallium had been purchased in one lot, rather than at different times, the problem would probably not have been solved. The low melting points of gallium alloys would permit centrifuge techniques, similar to that described here, to be used on various immiscible gallium-containing liquids.

B. W. Gonser (*Battelle Memorial Institute, Columbus, Ohio*)—I would like to stress the potential availability of gallium and the desirability of developing new applications. Although present in aluminum and zinc ores and some scattered sources in amounts suggesting a potential production in North America of some hundreds of tons yearly, difficulties in efficient extraction of the small percentage of gallium may limit practical exploitation to a fraction of this amount. Even so, potential availability, as uses develop, should be considered in terms of tons rather than grams or ounces. Likewise, the present high cost of several dollars a gram for small amounts is typical of most uncommon metals when first produced in the laboratory or on a small pilot-plant scale. Cost undoubtedly will drop drastically as higher volume production is warranted.

The properties of gallium, including its activity in alloying with practically all other metals, point to an interesting metal for metallurgical research. Such research should not be handicapped by the erroneous feeling that gallium is such a scarce and expensive material that it is not worth consideration practically.

R. I. Jaffee (*authors' reply*)—We would like to thank Dr. Denny for his detailed discussion. We acknowledge that supercooling of the gallium-rich alloys causes difficulty in obtaining accurate liquidus points. However, as the paper points out, we claim only ±2.5°C accuracy in the liquidus surface in this region. The ternary eutectic supercooled too, but an invariant point was always reached after solidification proceeded. We cannot agree with Dr. Denny that only the gallium-rich phase of the ternary eutectic was involved in the supercooling. If this were the case, in the Ga-Sn-Zn alloys for example, there would be no invariant point reached after solidification started, but a variable maximum temperature would be reached whose magnitude would depend upon the degree of supercooling and the amount of metal involved.

Dr. Gonser's points concerning the widespread occurrence of gallium in small quantities are well taken. The very high cost of gallium is directly related to its minute production. Undoubtedly the cost could be reduced sharply given a bonafide use and larger production.

Solidification Mechanism of Steel Ingots

by D. F. Rowe, F. A. Fisher, and W. A. Fiore

DISCUSSION, J. P. Nielsen presiding

M. S. Fisher and **D. R. F. West** (*Imperial College of Science and Technology, London, England*)—It may be of value to compare certain features of the results recorded in this very interesting paper with those of an investigation[2] involving determinations of temperature gradients and rates of solidification of steel blocks of 3 in. sq section, cast horizontally in sand molds, some of which contained chills.

Castings in plain carbon steels containing up to 0.8 pct C were made and, throughout this range of compositions, both inverse-rate and direct cooling curves, obtained from thermocouples placed within the mold cavity, showed a major arrest, the temperature of which was taken as the "effective liquidus" for the particular steel in question, solidifying under the conditions of the investigation. At the completion of the arrest, the curves showed a comparatively rapid decrease in temperature. Some of the steels investigated lay within the peritectic region, and a second arrest at 1485°C was detected. In Fig. 15, which shows the effective liquidus temperatures, the limit of the $\delta + \text{liquid}$ field has been placed at approximately 0.5 pct C. In inverse-rate curves corresponding to the thermal center of each casting, there was always a discontinuity, viz., an abrupt change of slope, at a temperature about 10° to 20°C below the "liquidus arrest," after which there seemed to be no significant irregularity in the rate of cooling. Curves corresponding to other positions in the casting generally showed some irregularities below the main arrest, probably as a result of heat flow from the solidifying interior. Even the reproducible discontinuity in the curves for the central positions appeared to have no theoretical or practical significance, though it probably corresponded to a stage in the solidification process at which only a relatively small amount of interdendritic liquid remained. Its temperature, rela-

tive to the liquidus, bore no apparent relation to the extent of the freezing range as indicated by the generally accepted equilibrium diagram, and hence it could not be regarded as even a "technical solidus" value.

The results of pour-out tests showed that the thickness of skin existing at a given time corresponded to the depth at which the liquidus arrest was completed. This means that at any given time a continuous network of crystals, no doubt containing a good deal of interdendritic liquid, but sufficiently coherent to hold together when the casting was up-ended, extended from the mold face to the position where the liquidus arrest was just about to end. The expression "start of freeze" wave, used by the authors in referring to the end of the arrest, is therefore liable to give a misleading impression, though it may not actually be wrong.

The liquidus temperature, as determined under any particular experimental conditions, is essentially that at which nuclei grow to a sufficient extent for the thermal effect to be detected. Effective liquidus temperatures as determined under sand and chill casting conditions were found to be lower than those given in the usual equilibrium diagram, the difference varying slightly for the various steels investigated, but being of the order of 10°C. The steels contained approximately 0.2 pct Si and 0.5 pct Mn, together with about 0.2 pct Ni and 0.05 pct Cr. It was estimated that the effect of these elements in lowering the liquidus values relative to those for pure Fe-C alloys was not more than approximately 6°C, so only part of the difference between equilibrium and effective liquidus temperatures could be accounted for in this way. The effective liquidus temperatures shown in the diagram are in good agreement with those determined by the authors for the steels employed in the work described in the present paper.

It is probable that even the liquidus values given in the generally accepted equilibrium diagram lie below the true equilibrium liquidus temperatures, and hence, under sand or chill casting conditions, when solidification eventually begins at the effective liquidus, a relatively large amount of solid can be formed, and thermal conditions are such that its formation is essentially isothermal. The effect is in fact one of undercooling, but no marked recalescence occurs, probably because the region of labile crystallization is not attained. The process occurs in the metastable region, in which crystallization proceeds only in the presence of inoculation. At the liquid-solid interface, where the liquid is liberally inoculated with the previously formed solid, crystallization proceeds as rapidly as the heat evolved is conducted away. In the central pool of liquid, only a limited amount of crystallization can occur around nuclei provided perhaps by nonmetallic inclusions or metal crystallites sinking from above.

An experiment showed a difference in the time for the completion of the liquidus arrest for a steel containing only 0.06 pct C and one containing approximately 0.6 pct C, both poured with the same degree of superheat, the time for the former being of the order of 30 pct longer than that for the latter. In the present paper the authors have clearly established this effect in noting differences in the "start of freeze" and "end of freeze" waves for steels of these compositions. The facts outlined here appear to have some bearing on this question. For the 0.06 pct C steel (see Fig. 15), the relation of the temperature of the liquidus arrest to the equilibrium freezing range indicates that, at the temperature of the former (approximately 1524°C), the percentage of solid that could form isothermally would be of the order of 60 to 80 pct. This can be only a very rough approximation, since the true equilibrium freezing range for these commercial steels is not known. For the 0.6 pct C steel, at its effective liquidus of approximately 1477°C, the amount of solid that could form would be about 10 to 30 pct. This estimated difference in the amount of solid able to form isothermally in the two steels cannot be correlated quantitatively with the duration of the respective liquidus arrests, but the fact that the difference does exist and is predictable, lends support to the view that the mechanism outlined may play an important role in the process of solidification of steel castings.

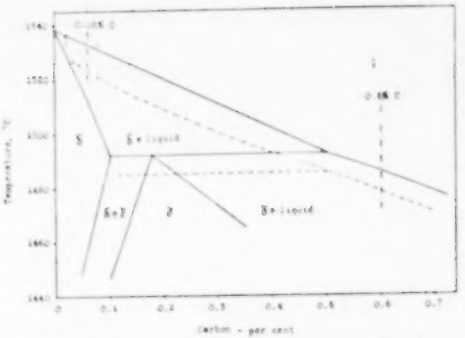

Fig. 15—Effect on equilibrium diagram temperatures of solidifying as commercial castings. Solid line—Equilibrium diagram for pure Fe-C alloys. Dashed line—Curves showing effective liquidus and peritectic temperatures for commercial steels solidifying in casting form.

There are, however, other factors to be considered. Although the study of solidification is basically a problem in heat transfer, yet the mechanism of solidification, particularly the part played by selective freezing, and the possible movement of segregated liquid and of crystallites, is important, not only in its effect on the macrostructure, but also in relation to the percentage of solid formed at a given temperature, especially when a particular region of a casting is considered.

H. F. Bishop, F. A. Brandt, and **W. S. Pellini** (authors' reply)—The detailed comments of Drs. Fisher and West relative to the interpretation and significance of thermal analysis data are appreciated. Inasmuch as the discussion pertains to the solidification of steel in sand molds it is necessary to consider the question of differences in the nature of the solidification mechanism as compared to chill (ingot-mold) solidification. This question has been discussed in other reports by the authors.[1,2] Briefly, the main difference in the mechanism of solidification for sand walls entails a long delay in the movement of the "end of freeze" wave due to the mild thermal gradients which exist through the solidifying mass as compared to the case of the chill wall. Thus, the "start of freeze" wave may move to the center of the section prior to the development of a completely solid skin at the surface. The relative rates of movement of the "start" and "end of freeze" waves is dependent on the width of the solidification temperature range. Fig. 16 illustrates the relative differences in graphic fashion. Insofar as the development of a liquidus hold and the movement of a "start of freeze" wave through the liquid is concerned, it is not necessary to differentiate between sand wall or chill wall solidification since there is no difference in mechanism. The only difference is in the time of existence of the hold and the rate of travel of the "start of freeze" wave.

We are in agreement with the finding that the liquidus hold does not occur at the equilibrium diagram temperatures. Our data indicates that the effec-

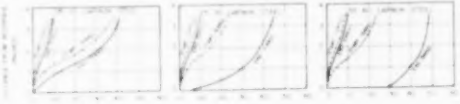

Fig. 16—Effect of rate of cooling and distance from interface on time required to start and complete solidification.

Fig. 17 (above)—Section through a 4 in. thick 0.30 pct C sand cast steel plate.

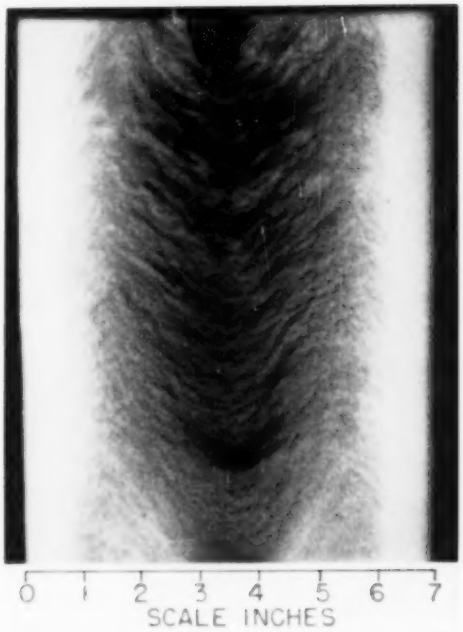

Fig. 18 (right)—Radiograph of the center of a sand cast pressure bled ingot.

tive liquidus is 10° to 15° F lower. However, we are not in agreement with respect to the solidus inasmuch as our data showed a corresponding effective solidus also 10° to 15° F below the equilibrium solidus line. It was accordingly concluded that the shift represented an alloy effect due to the presence of silicon and manganese.

The discussers' conclusion that the shift was not due entirely to an alloy effect unavoidably leads to a further conclusion that the liquidus hold is strongly suppressed and that a large percentage of solid may form isothermally during the hold period. It is difficult to conceive the gradual formation of solid in a strongly undercooled liquid as postulated, for such is in contradiction to the established nature of transformations of highly unstable systems. There is, moreover, direct evidence from the growth of columnar dendrites from the upper surfaces to the center in sand-cast plates or bars which indicates that the central region remains essentially as clear liquid during the hold period. Fig. 17 illustrates a section through the thickness of a sand cast, 4 in. thick plate of a 0.30 pct C steel, which required approximately 12 min for the columnar growth to reach the center (end of "start of freeze" wave). Dr. West shows similar photographs[7] for 4x4x16 in. bars and provides an excellent description of the mechanism by which columnar growth to the center occurs only from the top surface. The mechanism entails the movement of the upper surface dendrite tips into completely clear liquid while the lower surface dendrite tips are covered by small solid particles which tend to form just ahead of the advancing solidification front. Particles which form on the upper solidification front fall by gravity and settle on the lower surface. If the casting is reversed, the former lower surface reverts to columnar growth while the former upper surface now develops equiaxed structures.[7] In support of the clear liquid hypotheses of columnar growth, Dr. West[7] observed that, "The interior of the casting was not in a pasty state, since the drained liquid in the pour out tests flowed freely."

The failure of Drs. Fisher and West to detect a definite inverse rate solidus point related to the width of the solidification range also leads to their conclusion that the "technical solidus" determined by the authors is fictitious. The discussers, however, fail to recognize that the authors were successful in determining an effective solidus which was related to the equilibrium solidus. That this solidus value does in fact represent the point of essential solidity was proved repeatedly by pressure bleeding of sand castings at various stages of solidification. Fig. 18 presents a radiograph of a ¼ in. section removed from the center of a sand-cast 7x7 in. ingot which was pressure bled by forcing nitrogen gas into the casting 40 min after casting. The nitrogen gas displaced the interdendritic liquid at the time that the "end of freeze" point (determined by the technical solidus) had reached a 1 in. depth (see Fig. 16 "end of freeze" curve for a 0.60 pct C steel). The 1 in. thick solid skin formed at this time is clearly visible in the radiograph. It should be observed that at this time the thermal analysis predicts a semicoherent condition throughout the casting.

[7] D. B. F. West: "Mechanism of Solidification of Horizontal Steel Castings," Journal Iron and Steel Inst., 1950, 164, pp. 182-194.

[8] H. F. Bishop, F. A. Brandt, and W. S. Pellini: "Solidification of Steel Against Sand and Chill Walls," Trans. Amer. Foundrymen's Soc., 1953, 59, pp. 423-430.

[9] H. F. Bishop, E. T. Myskowski, and W. S. Pellini: The Contribution of Riser and Casting End Effects to Soundness of Cast Steel Bars," Trans. Amer. Foundrymen's Soc., 1954, 58, pp. 171-180.

[10] H. F. Bishop and W. S. Pellini: "Solidification of Metals," The Foundry, February 1957, 85, p. 87.

[11] "The Mechanism of Freezing of Horizontal Steel Castings," Journal Iron and Steel Inst., 1949, pp. 437-450.

Model for Dendrite Growth Form in Metals and Alloys

DISCUSSION, J. P. Nielsen presiding

A. Prince (*Imperial Chemical Industries Ltd., Billingham, Durham, England*)—The authors have observed the occurrence of the hexagonal structure in metals which have been solidified in a variety of ways. Recently we have observed what we believe to be a similar structure in an austenitic weld deposit of extra low carbon 18/10 Cr-Ni steel. The weld, a butt weld in ¼ in. material, was made by the argon arc

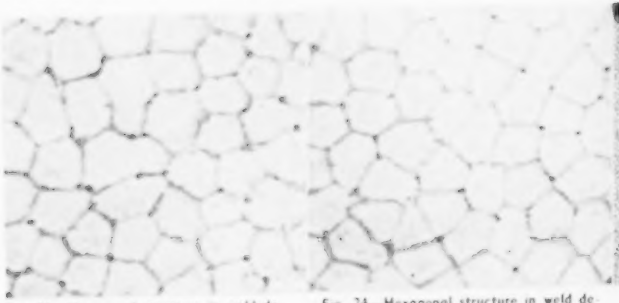

Fig. 23—Hexagonal structure in weld deposit of extra low carbon 18/10 steel. $FeCl_3$ etch. X500. Area reduced approximately 50 pct for reproduction.

Fig. 24—Hexagonal structure in weld deposit of extra low carbon 18/10 steel. $FeCl_3$ etch. X500. Area reduced approximately 50 pct for reproduction.

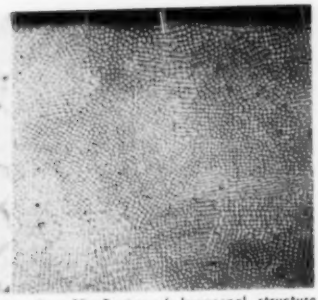

Fig. 25—Region of hexagonal structure in extra low carbon 18/10 weld deposit. $FeCl_3$ etch. X50. Area reduced approximately 50 pct for reproduction.

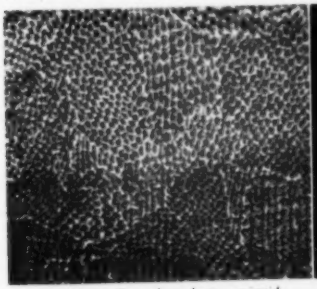

Fig. 26—Mammiform boundaries coinciding with the true grain boundaries. $FeCl_3$ etch. X100. Area reduced approximately 50 pct for reproduction.

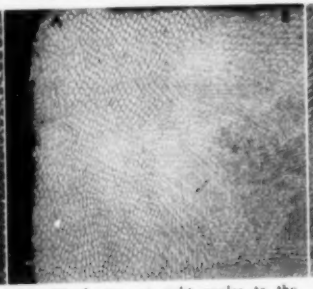

Fig. 27—Section at right angles to the plane of Fig. 25. Hexagonal structure still evident. X50. Area reduced approximately 50 pct for reproduction.

Fig. 28—Zone near weld interface of extra low 18/10 weld deposit. $FeCl_3$ etch. X100. Area reduced approximately 50 pct for reproduction.

process using filler wire of similar composition to that of the plate. Figs. 23 and 24 show the structure at high magnification and Fig. 25 the area at low magnification.

Fig. 26 confirms the fact that the mammiform boundaries form part of the grain boundaries in the appropriate places. The grain boundaries were brought up by rather deep etching in a 1:1 $FeCl_3$/methanol etchant. It will be noticed that the lower half of the micrograph is darker than the upper half. This is not an effect due to defective illumination; it is possibly an etching effect whose significance we cannot determine.

The curve given in Fig. 18 of the paper shows the expected correlation between mammiform size and rate of solidification. Apparently no results were obtained for sizes below 0.0075 sq mm. From Figs. 23 to 25 we have taken the average surface area of our mammiforms as 0.0005 sq mm. The weld metal solidifies very rapidly, as is well known, and, if we assume that a distance of $\frac{1}{8}$ in. has to solidify in the area where we found the mammiforms, then by taking an average time for solidification the rate can be deduced. For a solidification time of 2/3 sec the rate of solidification will be $3^3/_4$ to $2^1/_2$ in. per min. This seems, within the limitations placed upon an estimate of this nature, to be a reasonable confirmation of the authors' curve.

According to Messrs. Pond and Kessler a section taken at right angles to the section shown in Fig. 25 should show a striated pattern. Fig. 27 is such a section. It will be seen that along the edge *AB*—corresponding to the previous plane examined—the structure is still hexagonal. Can this be taken to mean that the mammiforms, in this case, grow in a very shortened form rather than in the elongated form, the cross branches also growing to a limited extent only? Mutual interference of the three dimensional cross branches could probably then produce a mammiform structure on any plane. This may be a particular case in that we find the phenomenon just described in the region of the weld metal where nucleation of the melt will tend to give an equiaxed structure (cf. Fig. 26). At the interface between weld metal and parent plate where the columnar structure is usually found, we noticed a transition type of structure in addition to the striated structure. Here, obviously, we are cutting across individual grains with variously oriented striae and getting the net effect shown in Fig. 28. That the mammiforms in the equiaxed region are not striated is interesting. Probably the authors would give us their views on the mode of occurrence of this structure. While discussing this topic it may be noticed in passing that Bengough sectioned his samples so that he could examine planes at right angles to each other. On both planes he observed his double cellular texture.

The final point is a comment on nomenclature rather than on observation on the admirable paper the authors have presented. The term mammiform is an ugly expression; why not refer to the structures obtained as a mosaic structure (cf. M. J. Buerger, ref. 3 in the paper)?

A. J. Goss *(University College, Southampton, England)*—The authors are to be congratulated on their important contribution to the study of the crystallization of metals. In the course of experiments in this laboratory, some of which were reported on briefly in a preliminary note[*] and in more detail at the Autumn Meeting of the Physical Society, London, in December 1951, observations of a line structure similar to that discussed by Pond and Kessler were made. Crystals of tin were grown at rates less than those used by Pond and Kessler, and, in agreement with these authors, a wider spacing of the lines was observed. For a rate of growth of 0.5 mm per min (0.02 in. per min) fine lines approximately 0.1 mm apart (as shown in Fig. 29) were found on the surfaces of some of the crystals of tin of 99.997 pct purity.

More recently the growth of single crystals of tin

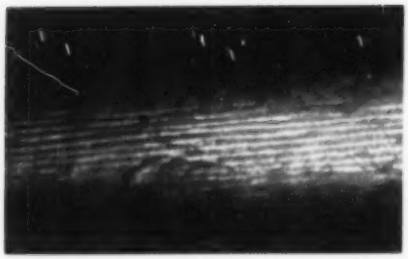

Fig. 29—Fine lines on surface of tin crystals. X10

containing accurately measured quantities of added metallic impurities has been studied. The line structure has been found to be considerably enhanced by these added impurities, the effect increasing with a higher proportion of impurity. In particular, 0.1 pct or 0.01 pct Ag and also 0.1 pct or 0.01 pct Cd or Zn or Pb have been shown to increase the line structure, while 1 pct Sb or In, which are more soluble in tin than the previous metals, resulted in tin-alloy crystals with broad lines on the surfaces. It has been concluded from these experiments that the impurity is the probable cause of these line structures, and, therefore, in tin of higher purity, no such structure would be formed. Smialowski[7] has obtained similar results for zinc and he was unable to find line structure in zinc of 99.999 pct purity.

B. Chalmers and **J. W. Rutter** (*University of Toronto, Toronto, Ont., Canada*)—According to its title, this paper is intended to explain the formation of dendrites in metals. The definition of a dendrite given by the *Metals Handbook*[1] is as follows: "A crystal formed usually by solidification and characterized by a tree-like pattern, composed of many branches; also termed 'pine tree' and 'fir tree' crystal." The micrographs presented by Pond and Kessler show a structure which appears to consist of rod-like elements, of hexagonal cross section, aligned approximately parallel to the direction of growth of the specimen. The end of each element terminates as a projection on the solid-liquid interface during growth. This structure certainly does not fit the definition given above and, therefore, should not be classed as dendritic. A recent publication[2] shows the form taken by dendrites in pure lead and the conditions necessary for their production.

The experiments reported by Pond and Kessler deal with the geometrical form of the structure which they investigated. In this respect, as well as in the omission of crystallographic and constitutional considerations, their observations are incomplete. For example, it was found that the structure may be regular or irregular, no experimental work is presented to show the factors which influence the regularity. Fig. 18 of the paper relates the average cross-sectional area of the elements of the structure to speed of solidification, without reference to the material to which it applies. The observed decrease in size with increase in speed is interpreted as due to an increase in the temperature gradient in the solid with increase in speed of solidification. Since the speed of solidification is controlled by the difference between the temperature gradient in the solid and that in the liquid, speed and temperature gradient are, in fact, two independent variables.

The observations made by Pond and Kessler are interpreted solely in terms of thermal considerations. In attempting to account for the existence of the structure, it is assumed that an array of projections is formed on a plane, growing interface. This is equivalent to saying that the plane interface is unstable. No reason is given to explain why this should be true. It is further assumed that these projections are stable, so that growth takes place at the same rate at the tip of a projection as at the base, although the temperature is higher at the tip. The only justification given for this assumption is to state that either the small mass of metal forming the projection can be heated above the equilibrium temperature of the interface, without melting, or that supercooling is necessary to cause the initial solidification and the temperature subsequently taken up by the tip of the projection is the true solidification temperature. This in no way explains why solidification can occur at the same rate at two points on the interface which are at different temperatures. On the basis of thermal considerations only, the projections should not be stable, but rather should disappear leaving a smooth, growing interface.

In a forthcoming paper,[3] it is shown that the impurities present in the material used play an essential role in the formation of this structure. More complete observations, based on thermal, constitutional, and crystallographic considerations, are presented. A theory is advanced which accounts for the existence and observed properties of the structure.

R. B. Pond (authors' reply)—It is most interesting to note the confirmation of some of our observations by the work of Dr. Prince with weld-metal deposits as evidenced by his excellent pictures. I believe that Dr. Prince has answered his own question concerning the appearance of the hexagons on faces taken 90° apart. If a solid solution exists and the specimen was sectioned so that the hexagonal net formed by the interference of the primary stalks of the dendrite was observable, at a 90° position the hexagonal interference figures of the secondary dendrite stalks might be seen or the line striae formed by the primary dendrite stalks, depending on the juxtaposition of the second cutting plane relative to the dendrite.

My thanks are also extended to Dr. Goss for the information on the effect of impurities on the dimensions of the line striae. It is noteworthy to report that since this paper was published the mammiform structure has been observed in solidified distilled water which had been deaireated. In view of this, I believe we might expect to find the mammiform structure in metals of infinite purity, although the observation might be most difficult to make.

Drs. Chalmers and Rutter have raised a number of points, and I wish to present the following answers.

The definition of a dendrite describes this form as a tree-like pattern; however, neither in definition nor in usage is there a differentiation between the segment of, and a total dendrite. That is to say, the twig of a branch, the branch of a limb and the limb of a tree all contain that periodic, appendaged form. The growth of a tree by the addition of these appendages or the morphology and location of the appendage is the characteristic of the "tree form." While it is true, we have not tried to analyze the total dendrite, we have given data and analysis relative to that element which we believe to be the dendrite growth form.

The curves relating to the average cross-sectional area of the mammiform to the speed of solidification, Fig. 18, refer to measurements on high purity tin.

Although the speed of solidification may be controlled by the difference between the temperature gradient in the solid and that in the liquid when these temperature gradients are not dependent on one another, there exists the case where the temperature gradient of the liquid is a function of the temperature gradient of the solid because the superheat and latent heat of fusion are removed from the liquid through the solid. In this special case which describes the conditions in the experimental apparatus used, the speed of solidification was found to be a function of the temperature gradient in the solid.

It should be noted that the use of supercooling of the liquid or superheating of the solid in explaining the mammiform site selection was not extended to the moving interface. The plane interface was shown to be stable when in equilibrium; however, once it began to move, it was not stable, but rather the mammiform was stable. This supported the assumption that the temperature of the surface of the mammiform was

everywhere constant, although there exists a temperature gradient down the axis of the mammiform. It should be further noted that although the rates of solidification for any two points on the mammiform are constant in the direction of movement of the total interface, they will vary according to the direction of movement of the true interface (interface of the mammiform with the liquid metal).

[7] Goss and Weindrush: Nature (London) (1951) 167, p. 349.
[8] Smialowski: Ztsch. Metallkunde (1937) 29, p. 133.
[9] Metals Handbook (1948) Cleveland: A.S.M.
[10] F. Weinberg and B. Chalmers: Canadian Journal of Physics (1951) 29, p. 382.
[11] J. W. Rutter and B. Chalmers: To be published.

Origin of Porosity in Castings of Magnesium-Aluminum and Other Alloys

DISCUSSION, J. P. Nielsen presiding

W. R. Opie (*National Lead Co., South Amboy, N. J.*)—In this paper the authors have clearly shown the relationship between gas precipitation during solidification and microporosity as found in resulting castings. I would like to point out that microporosity, or interdendritic gas precipitation, has a very marked effect on the physical properties of the cast metals.

In a commercial foundry, a completely gas-free casting is very seldom obtained. Numerous investigations have been conducted to show the effect of "pinhole" porosity upon physical properties. Metal with porosity in amounts that can just barely be seen with the naked eye has been compared with metal containing various amounts of gas porosity of the "pinhole" type that is clearly seen on machined casting surfaces. Results have generally indicated that the effect upon the physical properties of porosity varying in degree over the range commonly found in castings produced in the commercial foundry is negligible.

Fig. 16—Precipitation of a small amount of hydrogen during solidification forms interconnected interdendritic fissures. X500. Area reduced approximately 30 pct for reproduction.

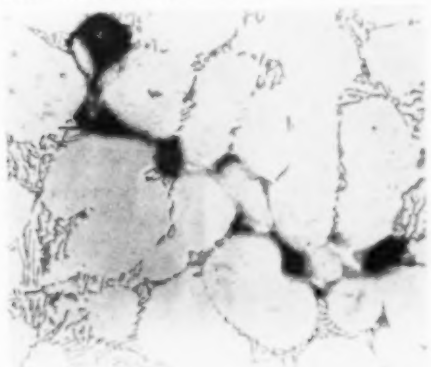

Fig. 17—As the amount of gas which precipitates during solidification is increased the fissures are widened. The result is pinhole porosity which is visible on a machined surface. X500. Area reduced approximately 30 pct for reproduction.

Fig. 18—Fracture of a test bar made from a 5 pct Si-Al alloy degassed with argon before pouring. There was no evidence in the microstructure of fissures. The fracture is intragranular. 33,200 tensile strength, 15.2 pct elongation. X5.

Fig. 19—Fracture of test bar of same alloy gassed with a small amount of hydrogen before pouring. The break is in part intergranular where it followed the fissures. 24,400 tensile strength, 6.2 pct elongation. X5.

Fig. 20—This material was gassed with moist hydrogen so that pinhole porosity resulted. Again the fracture follows the fissures. 21,200 tensile strength, 6.2 pct elongation. X5.

Deterioration of physical properties is caused by very small amounts of gas that cannot be seen by the naked eye on the machined surface. To illustrate this a 5 pct Si-Al alloy, melted in an induction furnace under controlled conditions and degassed before pouring into a silica flour mold by bubbling argon through the melt, had a tensile strength of 33,200 psi and an elongation of 15.6 pct in 1 in. Another melt made in a simular manner, except that a very small amount of hydrogen was bubbled through the melt before casting, yielded a test specimen with a tensile strength of 24,400 psi and an elongation of 6.2 pct in 1 in. A test specimen containing much more gas so that a pinhole type of porosity actually existed had a tensile strength of 21,200 psi and an elongation of 6.2 pct in 1 in.[7]

Fig. 16 illustrates the manner in which a small amount of precipitating gas weakens a 5 pct Si-Al alloy by forming hairline interdendritic fissures. In Fig. 17, a sample taken from a test bar containing enough precipitated gas to produce pinhole porosity, it can be seen that the larger volume of precipitating gas tends to widen the fissure. The formation of the

fissure can be accomplished by a very small amount of precipitating gas. The presence of fissures markedly affects the fracture. Three test bars having the same grain size but containing 1—essentially no gas precipitation, 2—enough gas precipitation to produce only hairline fissures, and 3—enough gas precipitation to produce pinholes have fractures as shown in Figs. 18-20, respectively. As can be seen the gas-free material appears much finer grained. The metal containing the fissures broke under less load through the weakened dendrite boundaries.

It is apparent that most commercial light metal castings contain enough precipitated gas to weaken them appreciably, as evidenced, for example, by the low tensile strengths and elongation values specified for a 5 pct Si-Al alloy (19,000 psi tensile strength, 6 pct elongation).[7] From these results it would appear that if we eliminate gas by controlled melting and casting we have a means of improving physical properties markedly. This would mean that the melt should contain less gas than can be held in solution in the solid metal.

E. J. Whittenberger and **F. N. Rhines** (authors' reply)—The authors wish to thank Dr. Opie for his interesting addition. The effects of porosity upon the physical properties and upon the pressure tightness of castings are a major reason for interest in casting porosity. It should be pointed out, however, that the attainment of high tensile properties by the near, or complete, elimination of gas is attended by certain penalties. First, as has been shown in the paper, the nearly complete removal of gas requires resorting to measures that would be difficult to make economical in foundry practice and, second, the control of shrinkage, in the absence of gas, would become so difficult as to make it impractical to produce many complex cast shapes, where adequate risers cannot be provided. On the whole, it would appear preferable to accept somewhat inferior tensile properties and to concentrate upon producing a uniform quality of casting, by holding the gas content between definite maximum and minimum limits, to be established individually for each alloy and each type of casting.

It may be pointed out, further, that merely limiting the gas content to its solid solubility limit is not sufficient to guarantee the absence of gas porosity. The "coring effect" may be expected to operate with gases, as with other solutes, and to bring about gas precipitation at much lower gross gas contents. The present experiments seem to indicate that the gas tolerance for producing a truly sound casting is almost zero.

The authors wish to correct a misleading interpretation presented in the text regarding the relative importances of water vapor and dry molecular hydrogen as sources of porosity in magnesium alloys. When Mg-Al alloys of the same composition were exposed to simular partial pressures of these two gases, c.f., 1.896 pct of porosity produced in a Mg-5.35 pct Al alloy by exposure to an argon atmosphere bearing 21 mm of water vapor, see Table III, and 0.65 pct of porosity associated with an alloy of identical aluminum content from the data for alloys exposed to an argon atmosphere bearing 15 mm of dry molecular hydrogen, see Fig. 11, it is apparent that water vapor exerts the stronger porosity producing influence. This observation, coupled with the fact that the partial pressure of water vapor is greater than that of molecular hydrogen in foundry melting room atmospheres, is in accord with the general belief that water vapor is the principle source of unsoundness in foundry operations.

[7] W. H. Opie: Doctor of Science Thesis, Mass. Inst. of Tech. (1946).

[7] Alcoa Handbook (1946) p. 625. Cleveland: A.S.M.

Mechanism of Grain Refinement in Aluminum Alloys

DISCUSSION, J. P. Nielsen presiding

F. R. Morral (*Kaiser Aluminum & Chemical Corp., Spokane, Wash.*)—The mechanism of grain refinement in aluminum alloys is not only of academic but also of practical interest. There appear to be two lines of thought to explain the mechanism, and the evidence presented seems to advocate each of them for the experimental conditions under discussion; although, they may be related as this discussion will show. Crossley and Mondolfo favor the peritectic reaction theory by which the intermetallic compound transforms into crystals of aluminum solid solution and thus seeds the melt with nuclei above the freezing point of aluminum.

Cibula[1] found that to have effective grain refinement the intermetallic compound should have a favorable crystal structure, or the interatomic distance between aluminum atoms in the intermetallic compound should be similar to that in the aluminum lattice. Typical of these are AlB$_2$ which was found more effective than TiC because it was a grain refiner even after superheating the aluminum. Combined additions of titanium and boron were more effective than each element singly. Combined additions of titanium and boron resulted in a coring of AlB$_2$ coated with TiB$_2$.

It seems significant that Cibula reported a grain size of approximately 400 grains per sq cm with only 0.02 pct TiC, while the authors had to add up to 0.25 pct Ti. Cibula obtained approximately 1900 grains per sq cm with 0.01 pct Ti and 0.001 pct B, while the authors obtained only 1000 grains per sq cm with 0.38 pct Ti. It is unfortunate that Crossley and Mondolfo do not state the actual amounts of titanium and carbon in the melts where both were supposed to be present.

The intermetallics to which Cibula referred were, conceivably, favorable to solid solution in aluminum if present in small enough amounts. If present in too large amounts they may actually have a detrimental effect because some other reactions may take place. Practically, however, the presence of carbon, boron, and possibly other elements, singly or in combination with metal elements—"solid impurities" as called by the authors—present in proper amounts appear to have, on the basis of the evidence presented in the literature, a grain refining effect.

F. A. Crossley and **L. F. Mondolfo** (authors' reply)—The differences in grain sizes reported by Cibula and the authors are most probably due to differences in cooling rates and to differences in purity of alloys. The grain size for a given titanium content decreases as the cooling rate increases. Grain size also decreases as the purity of the alloys decreases.

M. E. Eborall and **A. Cibula** (*The British Non-Ferrous Metals Research Association, London, England*)—The results described in this paper have interested us very much, particularly as the conclusions drawn from the work (which we have had the pleasure of discussing personally with Professor Mondolfo) differ so widely from our own.[1] In view of the firmness with which the authors express their views, however, we should have welcomed some explanation, in terms of their conclusions, of the results obtained by previous workers, many of which seem inexplicable if peritectic reactions are responsible for grain refinement. We have summarized some of the conflicting evidence in the next few paragraphs, before examining the significance of the present work.

The authors state that we concluded that the peritectic reaction had no important influence on grain refinement, mainly on the grounds that hyperperitectic chromium alloys were coarse grained. In fact, as is shown later, further strong evidence was also obtained from other alloy systems,[4] and a subsequent study[5] of undercooling in many different alloys supported the theory that the nuclei causing refinement were not crystals of the intermetallic compounds formed in hyperperitectic alloys.

For example, we have again and again shown that, both in pure aluminum and in Al-Cu alloys, titanium contents below the peritectic compositions produce almost the maximum grain refinement.[2-5] For example, it is shown in Table II of Eborall's paper[1] that 0.046 pct Ti will reduce the columnar structure of pure aluminum to a coarse equiaxial structure, and 0.125 pct Ti will reduce it to a fine equiaxial structure (0.45 mm grain diameter or less); Figs. 8 and 9 (Plates XLV and XLVI) and Table IV of Cibula's paper[2] show the large reduction of grain size in a 0.5 pct Cu alloy caused by only 0.01 pct Ti. All these compositions are hypoperitectic and it seems clear, from this evidence alone, that particles of $TiAl_3$ could not, even indirectly, be causing the grain refinement obtained.

The undercooling measurements in these alloys[2] confirmed that, where grain refinement occurs, effective nuclei are present in the melt, whereas, in castings which are not refined, such nuclei are absent. For example, a hypereutectic aluminum-1.3 pct Cr alloy, which was coarse grained, solidified after 2°C undercooling following the separation of the intermetallic compound. This indicated that nucleation by this compound did not occur, since 2°C undercooling was normal for unrefined aluminum alloys. On the other hand, aluminum containing as little as 0.003 pct Ti showed no detectable undercooling, indicating that strongly effective nuclei were present; it could only be inferred that particles other than $TiAl_3$ crystals were responsible for the refinement observed.

A further indication that the refining particles separate well above the Al-Ti liquidus temperature is provided by the results quoted in Table III of Eborall's paper.[1] Here it is shown that increase in casting temperature in the range 700° to 1000°C has a marked grain-coarsening effect far greater than that due to the corresponding decrease in the rate of cooling in the mold; the change affecting grain size therefore occurs in the crucible, at temperatures at which $TiAl_3$ crystals are in solution. The grain coarsening suggests that the nuclei dissolved by superheating remain in solution at the quite rapid rates of solidification in the mold, instead of reprecipitating. This interpretation is supported by the observation[1] that after the coarse-grained alloy is reheated to 750°C and cast, a fine grain size is obtained again and undercooling (which occurs after superheating) is once more eliminated. This can simply be explained by the reappearance of the nuclei, which separate out during remelting. Again, it is not possible to explain these results by assuming nucleation by $TiAl_3$, particularly as the titanium contents of some of the alloys were as low as 0.01 pct. Kondic and Shutt[6] observed very similar variations in grain size and undercooling in alloys of very low titanium content, which they, too, assumed were caused by titanium-rich nuclei.

We also showed[4] that very marked grain coarsening is produced in Al-Ti alloys, containing 0.12 to 0.29 pct Ti, when gases are bubbled through the melts at temperatures well above the liquidus temperatures. The compound $TiAl_3$, being in solution under these conditions even in the hyperperitectic alloy, could not have been removed as crystals from the melt; analyses confirmed that the loss of titanium from each alloy was 0.01 pct or less. The resulting metal of high titanium content remained coarse grained after various melting and casting operations in alumina-lined crucibles, presumably owing to the continuing absence of nuclei, but it could be refined again merely by the addition of high purity aluminum (which contains a trace of carbon), even though, as a result of dilution, the final titanium content was only 0.06 to 0.08 pct.

It can be seen from this discussion that our conclusions are based on much wider experience than that which the authors have quoted. We can only infer from these results that nuclei other than $TiAl_3$ crystals are responsible for refinement. No alternative explanation is offered in the present paper for the refinement observed in hypoeutectic alloys.

We note that the authors do, in fact, also assume that impurity nuclei were present in their melts, when explaining the grain coarsening produced by argon treatment. They imply that these particles are sufficiently numerous and effective to nucleate large numbers of $TiAl_3$ crystals but have no corresponding influence on the formation of solid-solution dendrites. We find this difficult to understand, particularly as previous work on Al-Ti alloys suggests quite the opposite; it has been shown that marked undercooling precedes the formation of $TiAl_3$ crystals[2-5] but the solid solution crystallizes without detectable undercooling whether or not $TiAl_3$ crystals are present.[5]

Our second conclusion, that the impurity nuclei responsible for grain refinement are carbide particles, was based on the following evidence.[4] First, we identified these substances in Al-Ti and Al-Ta alloys; specimens of these alloys from which the carbide particles had been removed by centrifuging or passing gases through the melt became coarse grained. Second, carbon additions to coarse-grained Al-Ti alloys, from which the original nuclei had been removed as described, restored the fine grain size. Third, all the known grain refiners except boron (for which an alternative explanation has been advanced) form carbides of the type identified in titanium and tantalum alloys; these carbides have structural and other properties which have been shown[7] to facilitate nucleation in other systems. Further confirmation has been obtained from the refinement produced by the very similar diborides formed by aluminum, titanium and other transition elements.[7]

In view of this weight of evidence, we think that the authors might well have examined the influence of carbon in greater detail, particularly as the grain coarsening observed in several of their experiments on carbon additions, which is said to disprove that this element is responsible for grain refinement, can be explained quite simply without assuming any reaction with the added carbon. In some experiments, the alloys were heated for ½ or 2½ hr at temperatures as high as 850° or 900°C, and under these conditions a considerable increase in grain size would have occurred even without the additions, as we have pointed out; this could have produced the observed results. It is, moreover, uncertain whether much reaction with the added carbon occurred in any of the experiments, because the tenacious oxide skin on molten aluminum normally makes it difficult to achieve contact between carbon and molten aluminum. We found in our own experiments that the addition of carbon to coarse grained Al-Ti melts was effective only when specific, highly active fluxes were used, and only then was full refinement obtained. If the flux used by the authors had been of this nature, the graphite crucibles would have rapidly disintegrated and we presume that they did not do so. Finally, even if extensive reaction with the added carbon did occur at the surface of the graphite or carbide particles, it cannot be assumed that they would have suitably dispersed in the melts; density differences might have caused rapid segregation, unless a superheating treatment had been employed to dissolve the carbide and reprecipitate it as fine particles. (It will be recalled that the refinement of magnesium-base alloys by carbon additions is only successful if suitable temperatures and fluxes are used.) The analyses show that, in the present experiments, no titanium was in fact removed as carbide particles. Was any direct evidence obtained that up to 50 pct or more of the titanium was converted into dispersed carbide crystals, as suggested in the paper?

It is probable, of course, that a number of substances may function as nuclei in aluminum alloys, differing in their effectiveness.[7, 8] Whatever the effective nuclei may be in commercial grain-refining processes, therefore, there remains the possibility that TiAl$_3$ crystals could have some, though a small, effect on the nucleation of solid-solution dendrites, particularly under the conditions of solidification used by the authors. The (tetragonal) structure of TiAl$_3$ suggests that this compound would not be a very suitable nucleus for aluminum. The authors suggest that the peritectic reaction can assist nucleation, but the reason for this is not clear; the thermodynamic potential of the peritectic reaction is zero at the peritectic temperature, like that of the liquid to solid-solution transformation, and it is known, in fact, that peritectic reactions in general, undercool considerably. Furthermore, the energy required for the formation of interfaces, which is the hindrance to crystallite formation, could hardly be influenced by the peritectic reaction. It is important to note that in all the hyperperitectic alloys in which marked refinement was observed by Isaac,[9] the structures of the primary and secondary solid phases were very similar (e.g., iron and copper in Cu-Fe alloys have face-centered cubic structures with almost equal lattice parameters); nucleation could, therefore, have occurred even in the absence of the peritectic reaction.

Turning to the experimental evidence put forward by the authors, we do not think it is by any means conclusive. First, the sharp changes in slope at the peritectic compositions in their grain-size curves are not justified; we, and several of our colleagues to whom we have shown the tracings of the ordinates and points of the authors' figures with their curves omitted, agree that only smooth curves can be drawn. The most that can be said, therefore, is that reduction in grain size begins in hyperperitectic alloys but only reaches a maximum at compositions above the peritectic point. This behavior is to be expected at low rates of solidification, such as those used by the authors, if impurity nuclei alone were responsible for refinement. At faster rates, the grain-size curves are of the same form but are shifted towards lower titanium contents; additions of a third alloying element, such as copper, and a reduction in casting temperature, have a similar effect on the grain-size curves, with no corresponding influence on the peritectic point composition. These effects are quite contrary to those predicted by the peritectic reaction theory and the authors could, therefore, quite easily check their conclusions by studying the above factors.

The metallographic evidence presented is, similarly, too limited to be unambiguous, as several alternative explanations, besides the authors', can be suggested for the coring observed round TiAl$_3$ crystals in an etched specimen. For example, at low rates of cooling, the TiAl$_3$ crystals might continue to dissolve in the nearby solid metal until it becomes locally saturated in titanium; the thickness of the surrounding titanium-rich zones would depend on the extent to which diffusion could proceed at the rate of cooling used. Thus, if the specimen is etched, coring would be seen round TiAl$_3$ crystals in addition to the normal dendritic coring of the solid-solution grains. Alternatively, a similar structure might be produced by concentration gradients established round TiAl$_3$ crystals growing in the melt; any crystallite formed near an existing, larger crystal would tend to grow away from it, into the melt of higher titanium content, and a dendritic pattern of concentration gradients would thus result. This would tend to persist in the solid metal, owing to the marked supersaturation required before the formation of TiAl$_3$ crystals,[7, 8] and would thus be imposed on the normal cored structure of the solid solution grains. Bohner[7] has shown similar structures which can be explained by means of the mechanisms we have suggested, and the present authors have not put forward sufficient metallographic or other evidence to discount these possibilities.

We have discussed this paper in some detail as we think it important to establish whether, in commercial refining processes, it is necessary to exceed the peritectic composition to obtain marked refinement. Furthermore the actual mechanism is of some importance in the development of grain-refining processes for other alloys; the authors may be interested to know that we have followed up our views in work on other alloys, with considerable success.

F. A. Crossley and **L. F. Mondolfo**—From the Cibula and Eborall remarks it seems that they have concluded that we are saying that the peritectic reaction is the only nucleating factor in these alloys. This is not at all our position. As our results indicate the peritectic reaction is a third factor which adds its effect to those of: 1—nucleation by impurities, and 2—restriction of grain growth by the concentration gradient mechanism.

Our observations of undercooling in Al-Ti alloys do not substantiate the contention that marked undercooling precedes the formation of a solid solution under all conditions of cooling as is implied by the discussers. We observed undercooling in only two cases of Al-Ti alloys having titanium contents above the beginning of the peritectic reaction content. Both of these alloys had been fluxed with argon. However, the other argon-fluxed peritectic alloys showed no undercooling. All Al-Ti contents exceeding the minimum amount necessary for the peritectic reaction showed halts at the peritectic temperature of durations of 10 to 30 seconds (100 g melts). The time of the halt was roughly proportional to the titanium content. This gave evidence that the peritectic reaction did take place, at least to a limited extent, at the surface of the primary TiAl$_3$ crystals.

Also, we found confirmation of the discussers' observations that no undercooling takes place in Al-Ti alloys of titanium contents below that required for the peritectic reaction. This, even in melts in which we scrupulously avoided the introduction of carbon. We believe nucleation and grain refinement in this range to be due to the mechanism proposed by Cibula and Eborall. We do not agree that TiC is the responsible nucleating agent. The melts of series 2 and 7 received identical treatments. They differ only in the type of crucibles used in the melting. The series 7 melts were made in alumina or coated clay crucibles, while the series 2 melts were made in graphite crucibles. The plotted results (Fig. 12 of the paper) show a significant effect due to the melting in graphite crucibles.

The discussers state that the thermodynamic potential of the peritectic reaction is zero at the peritectic temperature, like that of the liquid to solid transformation. This is true, but there is evidence that the amount of undercooling necessary to initiate the peritectic reaction in Al-Ti alloys is so small as to escape detection by ordinary thermal analyses. The recorder used in our investigations could detect temperature changes of 0.25 C, yet, generally, no undercooling was observed in Al-Ti alloys as we have reported above. Cibula and Eborall themselves report no undercooling in some liquid to solid transformations, and use this to support their proposed mechanism of grain refinement.

If impurity nuclei alone were responsible for refinement the grain size vs. composition curve would not have the shape that we found. Why should the grain size continue to decrease in the manner observed once the composition of beginning of the peritectic reaction has been reached? If impurity nuclei alone were responsible, alloys exceeding the composition of the beginning of the peritectic should behave similarly to the alloy composition just at the beginning of the peritectic and should exhibit much the same grain size—assuming equilibrium with respect to the liquid composition is extant at the peritectic temperature. This assumption seems a valid one under our experimental conditions. Figs. 8 to 10 and 14 indicate the large number of primary crystals that were formed and give evidence in support of this assumption.

Regarding the interpretation of the micrographs, evidence of nucleation by TiAl$_3$ is not only supported by Fig. 8, which shows dendritic structure, but by

Figs. 10 and 14 as well, which unequivocally show grain structure.

W. R. Opie *(National Lead Co., South Amboy, N. J.)*—The authors should be complimented on their systematic investigation of the grain refinement of aluminum. Their results seem to indicate that the refinement is associated with the peritectic reaction and not to very fine individual particles of the high melting intermetallic compounds acting as nuclei. However, I would like to describe a phenomenon which occurs in Y alloy foundry practice, which I have attributed to grain nucleation by submicroscopic particles of $TiAl_3$.

It is common practice in the casting of Y alloy (AMS 4220) to mix foundry scrap with an equal amount of virgin ingot, bring the charge to about 1200 F, bubble chlorine through for a short period to degas the melt, raise the temperature to the required pouring temperature for the casting being made, pour the charge into the pouring ladles, and pour the castings. About 0.15 pct Ti is contained in the virgin ingot which is usually enough to produce a fine grain in the resulting castings. Because of the chlorination step some of the titanium is removed. The remelted scrap, then, usually contains less titanium than is required to produce fine grain in slowly cooled thin sections. For heats made from large percentages of remelted scrap it becomes necessary to add titanium, and the time during which it is added in the melting and pouring cycle determines its effectiveness.

For example, if titanium is added in the form of a 5 pct Ti-95 pct Al master alloy to either the scrap remelt furnace, the melting pot before chlorination, or to the melting pot after chlorination, the resulting casting will be coarse grained. If the addition is made in the bottom of the pouring ladle and the metal from the melting furnace poured in on top of it, the casting will be fine grained providing the ladle is poured quickly. The difference in grain size between a casting made by using the ladle addition technique and castings made by adding the titanium during other parts of the cycle is very great. Castings made in baked sand molds which weighed about 70 lb would contain about 20 grains to the square centimeter if the titanium addition was made in the melting furnace after chlorination, but would contain about 800 grains to the square centimeter in the same thick section if the addition was made in the ladle. In both cases the total amount of titanium was 0.18 of which 0.15 pct was residual titanium and 0.03 pct was added.

The only explanation I can give for such a phenomenon is that the $TiAl_3$ constituents in the 5 pct Ti addition alloy are broken up and dispersed throughout the melt by the action of the molten metal dissolving the addition in the pouring ladle. They do not however, have time to go completely into solution before the metal is poured into the sand mold. Thus, being discrete submicroscopic particles at the time solidification commences, they act as nuclei and produce a small grained casting. It is to be noted that the amount of titanium used in the experiments described in this discussion is probably less than the amount necessary to form $TiAl_3$ by the peritectic reaction providing the system is in equilibrium.

F. A. Crossley and **L. F. Mondolfo**—The authors agree that refinement is produced by $TiAl_3$ particles. However, our principal contention is that these $TiAl_3$ particles are effective nuclei because of the peritectic reaction, which causes the surface layer of the particles to be transformed to a solid solution.

As far as the behavior of Y alloy castings, it must be remembered that in Y alloy iron, silicon, nickel, copper and possibly other elements are present. It is highly probable that 0.18 pct Ti does not produce the peritectic reaction in this alloy under conditions of equilibrium. But, particles of $TiAl_3$ would undergo the peritectic reaction (incomplete, however) whether or not the solution were in equilibrium. Also, there is

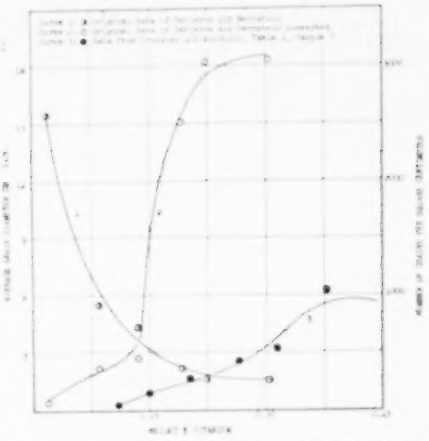

Fig. 15—Effect of titanium addition on the grain size of aluminum.

evidence that silicon will combine with titanium to form a complex silicide which does not react peritectically with aluminum. Given sufficient time, this reaction would render titanium additions ineffective for producing grain refinement. Thus, titanium added immediately before casting would be most effective in producing refinement.

Harold Bernstein *(U. S. Naval Gun Factory, Washington)*—A similar investigation which yielded different results and conclusions was described by DePierre and Bernstein.[7] They studied the effect of various additions on the grain size of commercial purity aluminum (99.81 pct). The results were expressed in terms of average grain diameter. For the sake of brevity, Fig. 15 has been prepared. It contains: 1—curve of average grain size of aluminum plotted against percentage of titanium added, from original data of DePierre and Bernstein; 2—curve of grains per square centimeter (converted from original data of DePierre and Bernstein) plotted against percentage of titanium added; and 3—curve plotted from data of Crossley and Mondolfo (Table I, Series 7). No. 1 is a smooth curve which approaches both axes asymptotically; curve 2 exhibits a change in slope coincident with a concentration of titanium of approximately 0.13 pct. Whether this reflects a metallurgical phenomenon or is simply the result of mathematical manipulations is open to argument. The difference between curves 2 and 3 is striking in two respects, maximum grain refinement achieved, and efficiency of titanium additions.

The experimental technique used by Crossley and Mondolfo is quite similar to that described by DePierre and Bernstein with one important exception—melt temperatures. The latter investigators used a constant temperature for all compositions, 730 C, while Crossley and Mondolfo varied the temperature with melt composition, reporting in one instance 900 C.

For the operation of the perifectic reaction, there are three requirements; a minimum concentration of added element, a minimum temperature, and conditions which permit the reaction to proceed. It may be assumed that these requirements have been met in the paper under discussion. It becomes obvious then from a comparison of curves 2 and 3 of Fig. 15, that the peritectic reaction is not the prime factor in grain refinement. The differences are evidently caused by the solution, at the superheating temperatures used by Crossley and Mondolfo, of the nucleating particles which were very effective at the lower temperatures used by DePierre and Bernstein. A clue as to the identity of the particles has been furnished by Cibula[8] in a very competent

theoretical analysis. The peritectic reaction should be undisturbed by other variations in melting practice such as repeated remelting and gassing the melt. Yet, there is a distinct attenuation of refinement in each case.

One additional point is in order. The exposure of an aluminum melt to carbon, either in the crucible itself, or by the introduction of aluminum carbide, does not necessarily mean carbon pickup by the melt. An analysis would be more convincing. Further, the data plotted in curves 1 and 2 were obtained from melts prepared in clay-graphite crucibles. The conclusion that carbon vitiates the grain refining ability of titanium is hardly tenable.

F. A. Crossley and **L. F. Mondolfo**—We are very grateful to Mr. Bernstein for bringing to our attention his results which so clearly support our thesis. The fact that our curve has much flatter slopes in all parts is probably due to differences in the maximum temperatures reached, differences in cooling rates, and differences in purity of alloys. Our alloys were heated to higher temperatures, were slower cooled, and were made from aluminum of higher purity than those of DePierre and Bernstein. All of these differences would tend to produce the observed differences in the two curves in the figure presented.

The peritectic reaction is not appreciably affected by variations in the melting practice, but the solidification of peritectic alloys is. Nucleation of the primary TiAl$_3$ crystals is dependent on the presence of solid impurities. Gassing, superheating, and fluxing, all affect the number and distribution of solid impurities, thus affecting the number and distribution of TiAl$_3$ particles, which in turn affect the secondary nucleation of solid solution.

In crucibles of graphite bonded with clay, the graphite at the surface tends to burn leaving a surface of pure clay. This, and the sluggishness of the graphite titanium reaction at low temperatures may account for the lack of noticeable reaction in DePierre and Bernstein melts.

J. Morgan (*Foundry Services, Canada, Ltd., Guelph, Ont., Canada*)—One of the main platforms of this paper seems to be refutation of an early contention by Cibula of the grain refining effect of titanium carbide and as this refutation seems to be now generally accepted we wonder if, while producing this excellent investigation into the peritectic reaction, the authors did consider the extension of their work a few stages further, especially in the light of modern knowledge of the combined effect of titanium and boron. This latter element was mentioned in the first paragraph of the paper but apparently merited no further discussion. In producing grain refinement, especially under practical foundry conditions, as a tool for the use of the foundry metallurgist, boron ranks equally with titanium, and more recent work by Cibula agrees that their combination produces the maximum effect. Again under production foundry conditions it is not always an easy or quick matter to add titanium by means of hardner alloys and losses make it quite difficult to add a calculated quantity. The writer is of the opinion that both these elements are better added in the form of balanced salt mixtures with agents to provide agitation. Without going into academic details, a simple summary of our opinion would be as follows: titanium on its own tends to coagulate and segregate especially if the metal is allowed to stand for any time; excess titanium will cause hard spots in the castings; if the metal is "stewed" at high temperature for some time most of the effect of titanium is lost because it becomes "soluble" in the aluminum and does not therefore provide nuclei, in the presence of boron a complex is formed which does not segregate to the extent of the simple titanium compounds (possibly due to specific gravity considerations); while excess boron would remove titanium from the melt in the form of a floating dross, the balanced amount of boron performs the function of lowering the solubility of titanium (in whatever form it can be present) in aluminum even at quite high temperatures and this makes available the maximum number of nuclei from the amount of titanium present.

F. A. Crossley and **L. F. Mondolfo**—We are very much interested in Mr. Morgan's observations since they confirm our experience in the foundry. However, we felt that no attempt should be made to add other complications until the mechanism of refinement by titanium was clearly understood.

P. G. England (*University of Birmingham, England*)—The shape of the grain-size composition curves obtained by the authors are of great interest but, although these offer strong support in favor of the peritectic theory, there are several experimental observations which are difficult to reconcile with this theory.

However, before dealing with these observations I would like to draw attention to one undesirable feature of the experimental procedure employed by the authors. It was stated that there were marked variations in grain size over the depth of the ingot and this is probably due to gravity segregation of nuclei or growing crystallites. By cooling unidirectionally from the base, however, the segregation can be largely overcome and an essentially homogeneous structure results. The method I am using is as follows, after the desired thermal treatment the melt is transferred to a preheated thin walled nickel crucible which is then cooled by standing it on a block of cast iron. Structures obtained by this method are far coarser than furnace-cooled specimens even with super purity aluminum, in spite of the faster rate of cooling.

The facts that the peritectic theory would appear to be unable to explain may be summarized as follows:

1—In order to coarsen the macrostructure of Al-Ti alloys by superheating, it is necessary greatly to exceed the liquidus temperature of the alloy. The superheat needed is 50°C in alloys low in titanium (0.002 pct) and 300°C in alloys rich in titanium (0.30 pct).

2—After superheating to such a temperature as will cause coarsening of the macrostructure and then holding, at a temperature below the coarsening temperature but still above the liquidus temperature, for periods of 1 hr or more, the fine structure is again obtained.

3—Aluminum is distinctly refined by as little as 0.002 pct Ti, an amount which is well below the amount needed to form TiAl$_3$.

Factors 1 and 2 may account for the abnormal increase in the number of grains on entering the peritectic range even if the carbide mechanism were in fact acting. At compositions exceeding 0.13 pct Ti, the liquidus temperature increases very rapidly and hence, also, the temperature to which the melts were superheated, since a superheating temperature of liquidus temperature, 100°C, was used throughout. Alloys containing small amounts of titanium would be taken above the coarsening temperature and any nuclei present destroyed. Cooling from the superheating temperature (approximately 765°C) to the liquidus temperature (approximately 665°C) would take only 17 min and insufficient time would elapse for the nuclei to be reformed. For alloys solidifying through the peritectic reaction, however, the coarsening temperature may not even be exceeded and if it were exceeded the higher superheating temperatures would result in a longer time of cooling to the peritectic temperature and so any nuclei that had been destroyed would have time to re-form. Hence alloys solidifying through the peritectic would be more likely to contain the normal number of nuclei than alloys of lower titanium content and hence the observed discontinuity in the grain size-composition curve may be more apparent than real.

These observations would appear to suggest that the explanation based on the peritectic reaction must be treated with caution, at least, until further experimental evidence is available.

F. A. Crossley and **L. F. Mondolfo**—Recent investigations have shown that high purity metals solidify with just a few degrees of undercooling when solid-

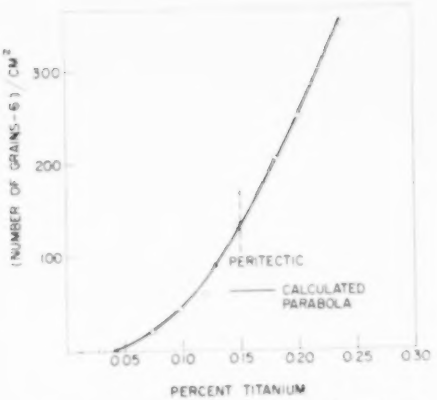

Fig. 16—Parabolic relationship of the effect of titanium on grain size.

ifying as relatively large masses of metal. When the metal is highly dispersed, undercooling of individual particles is considerable, the maximum being approximately one fifth of the melting temperature in degrees Kelvin." This behavior is attributed to the presence of solid impurities which nucleate the metal. These solid impurities are few in number in high purity metal. When a liquid metal of high purity is highly dispersed, many of the liquid particles are free of the solid impurities which nucleate. The result is the observed undercooling in highly dispersed metal. There is no reason to suppose that $TiAl_3$ should behave otherwise. Superheating of peritectic alloys destroys some of the solid impurities effective in nucleating the primary $TiAl_3$, the proportion destroyed being dependent upon the degree of superheating. It seems reasonable to assume that if the peritectic reaction has nothing to do with the resulting grain size, the grain size of the solid solution should become coarser with increasing alloy content, using the authors' melting practice. If grain refinement is due to the presence of some nuclei independent of the peritectic reaction, the nuclei will be the same whether the melt is poor or rich in alloy, e.g., titanium content. The melting point of these nuclei, especially, if a particular intermetallic compound as Cibula contends, will be the same no matter what the composition of the alloy. The coarsening temperature should be virtually independent of titanium content beyond a certain very small minimum content.

D. Turnbull and **J. H. Hollomon** *(General Electric Research Laboratory, Schenectady)*—Eborall and Cibula found that added titanium in amounts (0.05 pct) much less than required to give a peritectic reaction cause marked grain-size refinement. These results are (qualitatively at least) confirmed by Crossley and Mondolfo who find that the number of grains per square centimeter increases by a factor of at least 10 when the titanium content is increased from 0.03 to 0.12 pct. This range of composition is well below the peritectic composition of 0.15 pct. It is also noteworthy (Cibula) that the addition of only 0.01 pct Ti to pure aluminum virtually suppresses the undercooling of the melt. These facts cannot be explained by the peritectic theory but are consistent with Cibula's theory. From the foregoing evidence it must be concluded that the effect, if any, of the peritectic reaction on grain size is superimposed on another independent effect of the addition element.

The case for the peritectic mechanism rests largely on the supposed existence of a singularity in the grain size per square centimeter (n') vs. percentage of titanium (x) relation at a value of x near the peritectic composition x_p. According to the authors' description there is a discontinuity in the slope of n' vs. x at $x = x_p$. From a plot of log n' vs. log x it was established that the authors' data on titanium (Table I) could be described, within experimental error, by the parabola

$$n' = 6750x^2 - 12 \qquad [1]$$

from $x = 0.07$ to $x = 0.25$. For $x > 0.25$ the departure from eq 1 is serious. The calculated parabola and the experimental points [the authors seem to have plotted the nominal values of x; we have plotted the analytical results (col. 3, Table I) when given] are plotted in Fig. 16. Though, as the authors indicate, the data can be described satisfactorily by two straight lines intersecting approximately at $x = 0.12$ (cf. with accepted peritectic of about $x_p = 0.15$), they are just as well described by a single analytical relation, eq 1, with no singularity in the vicinity of x_p.

It is interesting that eq 1 implies a linear relation between x and the reciprocal of the average grain diameter. Since n, the number of grains per volume, is proportional to $n'^{3/2}$, it follows that n varies approximately as x^3.

The authors' data on the elements other than titanium are not extensive enough to accurately define x vs. n' relations.

We conclude that Cibula's main thesis, that marked grain-size refinement in aluminum is effected by nucleation catalysts formed in the melt by titanium and other elements, is supported by Crossley and Mondolfo's results.

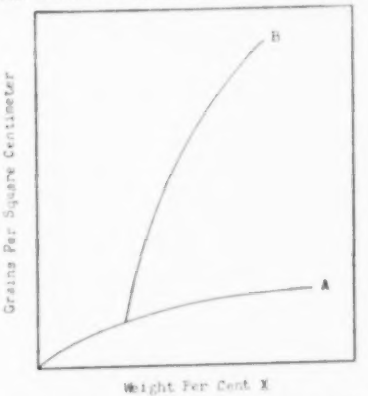

Fig. 17—Interpretation of grain size vs. composition data.

F. A. Crossley and **L. F. Mondolfo**—The lack of undercooling in some alloys has been commented upon in the reply to the discussion of Cibula and Eborall. The fact that the data fit a parbolic curve is perhaps coincidental; especially, since negative grain sizes are obtained for titanium contents below 0.04 pct using eq. 1. In our opinion the data should be interpreted as shown in Fig. 17. Curve *A* represents the effect of the concentration gradient mechanism; curve *B* represents the effect of the peritectic reaction. A curve of type *A* is clearly evident in the Al-Fe alloys, wherein no peritectic reaction takes place.

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On the Mechanism of Precipitation in Copper-Beryllium Alloys

DISCUSSION, J. P. Nielsen presiding

J. T. Richards (*The Beryllium Corp., Reading, Pa.*)—This interesting paper prompts several questions: 1—What is the effect of aging temperature on the formation of γ' and γ'' phases? Gruhl and Wassermann[7] have indicated a direct precipitation of the γ phase above 325°C. Below this temperature, they found an intermediate phase which subsequently changed into equilibrium γ. 2—What is the effect of cold work on the transition phases? Gruhl and Wassermann have observed direct precipitation to γ, independent of temperature, when the material was cold worked. 3—What is the possible influence of the γ' and γ'' phases on properties? For example, can the initial increase in resistance encountered at low aging temperatures be explained by the presence of γ' or γ''? 4—Would the authors care to express their opinion on the existence of an order-disorder relationship between the β and γ phases? Several English investigators[7] have suggested this possibility and it is not ruled out in the study of Gruhl and Wassermann.

A. H. Geisler (authors' reply)—Unfortunately the scope of this investigation was not of a magnitude to supply answers to most of Mr. Richards' questions. Thus, our answers can be based only on general principles supported by the work of Guy, Barrett, and Mehl on properties. We would expect that increased aging temperature and cold working would accelerate the formation of all precipitates. The hardening and increased resistance are associated with the formation of the coherent precipitates. Finally, in reply to the fourth question, there can be little doubt that γ is the ordered form of β Cu-Be.

[7] W. Hume-Rothery, P. W. Reynolds, G. V. Raynor: Factors Affecting the Formation of 3:2 Electron Compounds in Alloys of Copper, Silver, and Gold. Journal Inst. Metals (1940) 66, pp. 191-207.

Metallurgical Mechanism for Mercury Stress Cracking of Copper Alloys

DISCUSSION, J. P. Nielsen presiding

W. R. Hibbard, Jr. (*General Electric Co., Schenectady*)—Ikeuye and Smith[8] have shown that the dihedral angle changes with temperature if the composition of the liquidus changes. Hansen[9] shows (tentatively) that the composition of the liquidus of the Cu-Hg diagram changes significantly between room temperature, 170°, and 350°C. Since the Zn-Hg changes also, it may be expected that the composition of the liquidus between brass and mercury would change between room temperature and 350°C. Therefore, it appears that the equilibrium dihedral angles between copper or brass and mercury should decrease with increasing temperature, contrary to the statement at the top of p. 1191 of the paper. The small dihedral angle found at 350°C for brass and mercury was not found at 170°C and would not be expected necessarily at room temperature. At these lower temperatures the angle should be larger, possibly exceeding 60°. Therefore the experiment presented is considered inconclusive regarding the role of the dihedral angle in mercury cracking of brass at room temperature.

In addition, the role of the zinc-containing intermetallic compound is uncertain, e.g., the compound is not visible in Fig. 4, although fracture has occurred, and the compound is not resolvable along all boundaries of Figs. 2 and 3. The composition of the compound is not known. Finally, it is difficult to see how stress can cause continued contact of the alloy with mercury. When fracture occurs, it does not appear to open up fresh alloy surfaces, because the unamalgamated surfaces do not crack. The basic theory is attractive but the details lack experimental evidence.

[8] K. R. Ikeuye and C. S. Smith: Trans. AIME (1949) 185, p. 762; Journal of Metals, October 1949.

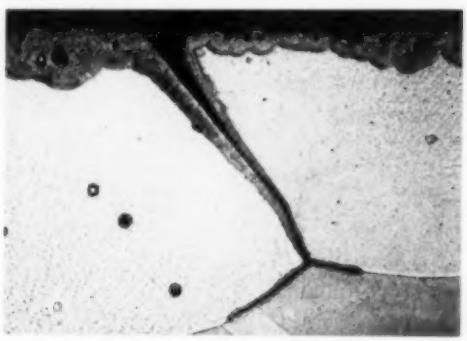


Fig. 5—Brass (69 pct Cu) annealed at 850°C, immersed in mercury at 350°C, and bent at room temperature after removal of the mercury.

W. D. Robertson (author's reply)—The points raised by Dr. Hibbard are pertinent and are being investigated as a result of the initial work reported in the paper. Regarding unresolvable grain boundaries, perhaps Fig. 5 is more illuminating. It was taken from the specimen shown in Fig. 3. The fracture illustrated was produced by bending after mercury was removed in vacuum. It appears that grain boundry diffusion is involved and that the difference between the results at 170° and 350°C may be explained in part by insufficient time at the lower temperature. Rather than speculate further about the mechanism at this time, we are undertaking to obtain the necessary data to separate the variables involved.

Preferred Orientation in Zirconium

DISCUSSION, J. E. Burke presiding

P. A. Beck (*University of Illinois, Urbana, Ill.*)—The results presented in this paper for cross-rolled and annealed zirconium are particularly interesting, since they show much more clearly and definitely than it was ever shown before the reorientation that takes place upon annealing in a cold worked hexagonal metal. Since both the cross rolling texture and the corresponding annealing texture represent essentially single orientations (with scatter), the authors' interpretation that the reorientation may be described as a

30° rotation around the hexagonal axis appears to be well substantiated, as far as their data go.

As pointed out earlier,[7] and also by the present authors, this reorientation is entirely analogous to that generally encountered on annealing of face-centered cubic metals. In both cases the rotation is around an axis perpendicular to the closest packed plane, and the extent of rotation is such as to lead to maximum disorientation between the growing grains and the matrix. For this particular relative orientation, where the surface energy is at a maximum, the boundary mobility is greatest, because the rate of self-diffusion along the boundary is highest.[8] Thus, the authors' findings are in excellent agreement with the view, according to which annealing textures are determined by the orientation dependence of boundary mobility (oriented growth theory) and the latter in turn is a result of the orientation dependence of self-diffusion rates in grain boundaries.

F. D. Rosi (*Sylvania Electric Products Inc., Bayside, L. I., N. Y.*)—The authors should be complimented for their welcomed data on the textures of zirconium. With regard to an analysis of these textures, it is interesting to point out that a significant difference exists between the rolling textures of the common hexagonal close-packed metals; and this difference appears to be related to the difference in the values of their c/a ratios. Thus, in titanium, zirconium, and beryllium (which show negative deviations from the ideal c/a ratio for closest packing, 1.633) the cold-rolled texture may best be described as one in which the [1010] is parallel to the rolling direction and the (0001) plane is inclined approximately 25° to the rolling plane in the transverse direction. The essential difference between this texture and that for zinc and cadmium (which show large positive deviations from the ideal ratio) is in the direction of tilting of the basal planes, which for the latter is in the rolling direction. In the case of magnesium (whose c/a ratio is close to the ideal value) the basal plane coincides with the rolling plane and may be considered as occupying an intermediate position.

The difference in the textures of these c/a grouped metals strongly suggests that their crystallographic mechanism of plastic flow is also different. In this respect, recent studies at our metallurgical laboratory indicate that the plastic behavior of hexagonal close-packed metals with c/a ratio less than the ideal can be quite different from that generally associated with metals of this structural class, namely magnesium, zinc, and cadmium. In titanium, for example, slip was found to occur predominantly on the prismatic planes type I, while twinning was observed on three distinct types of pyramidal planes. Recently acquired results on the deformation of zirconium also suggest a mechanism of plastic behavior similar to titanium. Therefore, it is apparent that the mechanism of plastic flow in titanium and zirconium, of similar axial ratio, is not only different from that of zinc and cadmium, but also much more complex. Furthermore, twinning appears to play a more important part in the deformation of titanium and zirconium.

The foregoing, therefore, has been presented simply to acquaint the authors with the complexity of the problem of correlating the observed textures with the plastic behavior in zirconium, as well as the danger of drawing analogies with the textures of cadmium and zinc.

R. K. McGeary and **B. Lustman** (authors' reply)—An X-ray spectrometer has been used by the authors to establish with a high degree of accuracy the angular relationships associated with the reorientations of single and double-textured cold rolled zirconium upon annealing. With regard to this work, which will be published soon, it can be said that in no case are the results inconsistent with the ideas suggested by Dr. Beck.

The marked differences in published pole figures of the metals beryllium, titanium, and zirconium of c/a ratio less than ideal when compared to those of zinc and cadmium with c/a ratio greater than ideal is good evidence that the elementary deformation elements of the two groups of metals are different, as pointed out by the authors in the paper, and also by Dr. Rosi in his discussion. That the pole figures obtained on deformation are sensitive to the single-crystal deformation elements and may, if they are known, be derived from them quite successfully, has been shown in a recent series of articles by Calnan and Clews.[9]

[7] P. A. Beck: Theory of Annealing Textures. *Trans.* AIME (1951) 191, p. 475; JOURNAL OF METALS (June 1951).

[8] E. A. Calnan and C. J. B. Clews: Deformation Textures in Face-centered Cubic Metals. *Philosophical Magazine* (1950) 41, p. 1085; Part II. Body-centered Cubic Metals (1951) 42, p. 616; Part III. Hexagonal Structure (1951) 42, p. 919; The Prediction of Uranium Deformation Textures (1952) 43, p. 93.

Preferred Orientation of Arc-Cast Molybdenum Sheet

By M. Semchyshen and C. A. Tavares

DISCUSSION, J. E. Burke presiding

P. A. Beck (*University of Illinois, Urbana, Ill.*)—An interesting result of this work is the fact that in cold rolled molybdenum sheet complete loss of work hardening is obtainable on annealing, without change in texture. The retainment of the cross-rolling texture on soft-annealing is particularly significant, since this is essentially a single orientation texture, where texture retainment could be achieved by only one of the two mechanisms which produce this effect in aluminum,[7] namely by recrystallization in situ.

Recrystallization in situ was originally discovered by Collins and Mathewson (1940) and by Crussard (1944) as a phenomenon taking place on annealing in relatively mildly deformed single crystals of aluminum. It now appears to be a major (in many cases the major) mechanism of annealing of severely cold rolled polycrystalline material, not only in aluminum,[8] but in metals as different in character as beryllium,[9] titanium,[10] and molybdenum. All these data now confirm the general validity, at least for more or less pure metals, of the interpretation of the annealing process given a few years ago by Smith.[11] The whole question of recrystallization is now reopened. Indeed, it appears that recrystallization, as defined traditionally, may not occur at all, since at the time "deformed material" is absorbed by "recrystallized grains," it has already become completely strain free by recovery and "recrystallization in situ."

[7] P. A. Beck and H. Hu: Annealing Textures in Rolled Face-Centered Cubic Metals. JOURNAL OF METALS (January 1952); *Trans.* AIME, p. 83.

[8] A. Smigelskas and C. S. Barrett: Preferred Orientation in Rolled and Recrystallized Beryllium. *Trans.* AIME (1949) 185, p. 145; JOURNAL OF METALS (February 1949).

[9] H. T. Clark, Jr.: Textures of Cold-Rolled and Annealed Titanium. *Trans.* AIME (1950) 188, p. 1154; JOURNAL OF METALS (September 1950).

[10] C. S. Smith: Discussion on P. A. Beck: Orientation in Recrystallization and Grain Growth. *The Physics of Powder Metallurgy* (1951) p. 50. New York: McGraw-Hill Book Co.

DISCUSSION, D. C. Jillson presiding

C. H. Mathewson (*Yale University, New Haven, Conn.*)—The authors argue, chiefly on the basis of directional peculiarities of Laue spots after extension, that all slip in their molybdenum crystals was on dodecahedral planes in the close-packed direction. This basically would seem to call for a subdivision of the orientational space into triangular areas like the two shown in Fig. 1, each prescribing slip on a single most highly stressed system. On the contrary, they find a variety of single and combined slip behaviors in the basic triangle, which points to some unknown complexity in the process of deformation. It would appear that many more experiments will be necessary before this is understood.

They demonstrate rotations about axes generally lying in the chosen slip plane and normal to the slip direction, which correspond to the elongated patterns of the Laue spots, but in the complicated cases where a predicted type of slip did not occur, the rotations derived from the shapes of the Laue spots do not always fit too well with the observed movements of the axis. For example, in Fig. 8 for crystal No. 12, the best expression of the first step in the deformation would be to combine I-C and II-A, just as was done in Fig. 11 for crystal No. 25, and not I-C and III-C, based on the shapes of Laue streaks. To me it seems rather forced to make the detailed interpretation of these streaks indicated in Fig. 10. Incidentally, the major trend of the streaks is denoted III-C in Fig. 10, and designated as a minor effect in the projection of Fig. 8.

All in all, the authors deserve commendation for directing attention to the value of the strain indications of the Laue pattern for identifying probable slip systems, but this in the writer's opinion needs much more study and elaboration before it can be used with great assurance in cases of complex deformation.

F. L. Vogel, Jr. and **R. M. Brick** (*University of Pennsylvania, Philadelphia*)—It has long seemed peculiar that body-centered cubic metals should choose planes of low packing density when at least one of the relatively densely packed {110} planes would be favorably oriented for shear. The authors are the first to advance well documented evidence to support the contention that glide markings on {112} or {123} planes are not real but spurious and that slip really had occurred on {110} planes.

The analysis of Greninger, to which reference is made in this paper, explains "spurious" {112} or {123} slip in body-centered cubic metals by cooperating {110} slip systems. The wavy character of the slip lines is attributed to variations in the relative contribution of each {110} plane to the glide process.

If this analysis is correct, then there will exist an orientation of the stress system with respect to the crystal axes wherein, of all of the planes containing the slip direction, a {110} type bears the maximum shear stress. Now, since the resolved shear stress is greater on this {110} plane than on any other {110} plane, or combinations of other {110}'s, if it is assumed that slip takes place solely by {110} slip, then only one plane will operate in this case. This should result in the type of slip lines observed in face-centered cubic metals, i.e., lines which are straight regardless of whether viewed perpendicular or parallel to the plane of the slip direction and stress axis. Further, if it is assumed that slip is confined to the {110} planes there should appear an increase in the waviness of the slip lines as the plane of apparent glide varies from {110} to {112}. Evidentally this logical result of this analysis is not borne out by the observations.

R. Smoluchowski (*Carnegie Institute of Technology, Pittsburgh*)—The very interesting work of Chen and Maddin indicates clearly how difficult it is to obtain conclusive experimental data on slip mechanism in cubic body-centered lattices. In continuation of Dr. Opinsky's and my own work on Fe-Si alloys a more complete theoretical consideration of the critical shear stress in terms of dislocations theory has been made and will appear shortly elsewhere. It may be pointed out here that the well-known Andrade relationships quoted by the authors do not seem to hold for nonalkali metals as is indicated by Table III. In fact only sodium is in definite disagreement with theoretical considerations. This difference is presumably due to the important role of ionic core repulsion in nonalkali metals as compared to the preponderant role of electronic configuration in the alkali metals. It is possible to account, in a semiquantitative way, for the temperature and composition dependence of slip mechanism in body-centered cubic metals.

Table III. Slip Planes in Body Centered Cubic Metals

T/T$_m$	Na	K	W	Mo	Fe*	Fe-Si	β CuZn
0.00-0.24	112	112	112	110 112 123	110 112 123	110	?
0.26-0.50	110	110	110	110	110 112 123	110	110 123
0.50	123	123	—	?	—	110	?

* At temperatures lower than 0.08T$_m$, only the {110} plane is active in iron and in Fe-Si alloys with less than 2.5 atomic pct Si.
† More than 2.5 atomic pct Si.

A. J. Opinsky (*General Motors Corp., Detroit*)—The authors are to be commended for their paper. The renewed interest in this field is very encouraging. In the third element under "Determination of Slip Elements" the authors state that "the slip lines were quite straight and uniformly dispersed . . ." How do they then justify the later statement, in the sixth paragraph of "Discussion," that "the slip traces in body-centered cubic metals are inherently wavy?" It is true that the first statement was made concerning the beginning of deformation, but how can an inherently wavy line be straight at any time?

It was also the discusser's experience that the slip lines at low deformation were straight, and in his work an effort was made to keep the deformation as low as possible and still have visible slip lines. The resolved shear stress-critical shear stress theory holds, strictly speaking, only for the initiation of slip, for complications may be introduced by further extension. How much of the data presented by the authors applies to the really early stage of slip? For instance, how great was the first extension for M-12? What was the extension upon which the data for M-25 are based? Consider a crystal which has been strained just beyond the point of first yield: only a few slip bands will be observed. Hardly any rotation could have taken place, and very little asterism would occur. Would not the X-ray method of this paper be of limited or no value under such conditions? These are the conditions that must be known first before going to higher strains.

In Fig. 11, how can slip plane III be said to operate if axis of rotation III-C was not observed? No combination of I and II could be expected to yield the slip traces observed between I and III.

The third conclusion of this paper is almost correct, but would be more precise if modified to state: "An explanation based upon systems of highest resolved shear stress does not appear to be complete. . . ." The other necessary factor is critical shear stress. There seems to be no satisfactory *a priori* reason to limit the number of possible slip planes; the high atomic density

hypothesis serves merely as a guide. The introduction of the concept of critical shear stresses presents a possible avenue of attack on the problem of the number of planes operating. High index planes do not operate because their critical shear stresses are too high. Proper low index planes above {110} may or may not be operative, depending on temperature and composition. In other words, their critical shear stresses may be close enough to that of {110} that they can operate in some instances.

The authors were trying to prove the third conclusion when they plotted data on the maximum resolved shear stress triangle. However, it would be best not to follow this procedure, for it tends to be confusing. The data should be plotted on a blank stereographic triangle and conclusions drawn therefrom.

R. G. Treuting (*Bell Telephone Laboratories, Murray Hill, N. J.*)—Amidst the wealth of data in this interesting paper there is a small but possibly quite significant item on which the authors may choose to comment further. This appears in Fig. 2, which shows Laue back-reflection photograms of specimen Mo-13 before and after plastic extension. A spot near the center, in the upper right hand quadrant, at the intersection of several tautozonal curves, seems greatly increased in intensity after yielding. The authors have privately confirmed that this is a {100} reflection.

Increase in integrated diffracted intensities of strong lines from reduction in primary extinction has been observed in powder patterns from brass filings by Averbach and Warren.[1] Although the peak intensities are reduced, the lines are broadened by cold work to a greater area. The line of the presumably active slip plane, {111}, does not seem particularly favored in this respect by other than its position as strongest. In X-ray micrographs of the Barrett type, it is found that slip lines reflect more intensely;[2] it has been suggested that a contributing cause may be faulting incident to slip.[3] In such photographs the reflecting plane is not necessarily, or even probably, of the slip system.

Although this {100} reflection may have become intensified from other causes (e.g., shift of the plane on extension to an angle with the incident beam permitting characteristic reflection), it seems pertinent to inquire whether it can yet be established that the intensification is directly attributable to the deformation, through some such mechanism as suggested here, or another.

In this connection it is interesting that the one spot seems intensified so much more than the others registered. In taking X-ray micrographs of a slipped aluminum crystal, the writer has observed that slip lines were more intensely reflecting regions irrespective of the particular reflection used to record the image. If it be due to faulting along the slip plane, this demonstrates the three-dimensional nature of such a fault. Then why in this case were the other spots not likewise intensified? It may be that they were—certainly there are other changes in spot densities shown here, some relatively weakening—and that there is some relation between the intensity change and inherent intensity as in the powder patterns of Averbach and Warren. A satisfactory answer must await further experiment, but in the meantime the authors' opinions would be of interest.

N. K. Chen and **R. Maddin** (authors' reply)—Dr. Mathewson points out that many more carefully documented experiments are needed before the unknown complexities in the deformation process can be understood. We might add here that very careful studies are being made on body-centered cubic metals, i.e., molybdenum, tantalum, niobium and tungsten, at Johns Hopkins University with regard to: 1—the progressive formation of slip lines, 2—the role of the deformation band, 3—the structural alterations as determined by X-rays, 4—electron microscopy, and 5—multiple beam interferometry. The results of these studies will be reported at some later date.

Unfortunately, there is a misrepresentation in Fig. 10—III-C should be designated I-C and vice-versa. With respect to Fig. 8, the stress axis rotation from position 0 to 1 is less than 2°, and the accuracy of orientation determination is ±2°. Consequently, the true position 1 can possibly be along a great circle course with positions 0 and 2. Under these conditions I-C and III-C would accurately describe the apparent action.

Drs. Vogel and Brick bring out two interesting points with respect to waviness of slip lines and crystal orientation: 1—if slip takes place solely on a (110) plane, slip lines should be straight, regardless of the plane of observation, 2—as the plane of apparent glide varies from (110) to (112), there should appear an increase in the waviness of the slip lines. It should be stated, however, that these two expectations may not necessarily be fulfilled since some additional assumptions made underlying these expectations may be in doubt irrespective of the present analysis of the slip process. First, the waviness of slip lines may not be entirely due to slip on cooperating slip planes; other causes, such as lattice rotation during deformation, formation of deformation bands or mechanical twins and probable rotation of the lattice about the stress axis, etc., should also be considered. Second, in the case of slip on cooperating {110} planes, the magnitude of the relative contribution of each (110) plane may be as small as a few atomic distances and hence any difference resulting in the macroscopic wavy character of the slip lines may not be resolved. Also, there may be nonuniform variations in the participation of each (110) plane to make up an integrated slip trace.

Nevertheless, it would seem that the real character of waviness may be more advantageously investigated under the electron microscope or by means of multiple beam interferometry. In this respect, it can be pointed out that when wavy slip bands are produced in aluminum after moderate or large deformation, Wilsdorf and Kuhlmann-Wilsdorf[4, 5] were able to show with electron micrographs that: "in spite of their non-crystallographic appearance they, in reality, are formed by exceedingly fine multiple slip" on (111) planes.

Unfortunately, it seems that Dr. Opinsky did not realize the well-known variable involved in the observation of slip lines, i.e., the relative position of the observation surface with respect to the slip direction. It is commonly known that in body-centered cubic metals, the slip lines may be straight or wavy depending on whether the observation surface is parallel or perpendicular to the slip direction. This is also true at low deformation, though the waviness at positions perpendicular to the slip direction as witnessed by the very faint striations is not so pronounced compared to the slip lines after their full development. This point, if properly understood, should avoid the confusion brought out in the discussion by Dr. Opinsky.

The deformation used in the optical determination of slip planes was generally below 3 pct extension. To determine the slip direction by axis rotation, the deformation was greater. However, an alteration of the Laue spots, indicating the initial stage of "asterism," was observed when all the specimens were extended to just beyond their yield.

In Fig. 11, although the axis of rotation III-C was not observed, I-C was observed. In order that the apparent glide on (112) or (123) was to be explained on the present analysis of the slip process, plane III was believed to have operated. The operation of slip plane II was considered equivalent to the action of "conjugate slip" in face-centered cubic metals.

The resolved shear stress-critical shear stress hypothesis, in order to be conclusive, should wait for more carefully documented data on the determination of slip systems in body-centered cubic metals. For instance, with respect to a specific crystal orientation, the exact slip plane and direction should be listed along with deviations from the ideal positions. In this respect recent work by Vogel and Brick[6] has indicated the great complexity of slip planes in iron and the apparent behavior of noncrystallographic slip. If the

hypothesis of critical shear stress is to be applied, it would seem that not only (112) or (123) but all planes in the zone containing the slip direction should be considered.

Dr. Treuting's comment on the intensification of the Laue spots in Fig. 2 is of great interest. We have puzzled about these intensity changes, but have been unable, so far, to assign any particular mechanism to account for them. It appears to us that herein is a clue which, when properly evaluated, should result in enhancing our understanding of plastic deformation. It can be pointed out, however, that, since the intensification is accompanied by an alteration of the shape of the spots, i.e., the initial stage of "asterism," it can be concluded that the range of orientation must also have increased after deformation. A similar observation in the case of aluminum can be noted. Here, the presence of a deformation band has been shown to be the cause of asterism at the early stage of deformation.

Certainly, it is realized that the intensities of Laue spots do not depend upon the crystal structure alone, but also are influenced by: 1—the strength of the particular component in the X-ray beam to which each reflection is due, 2—each spot may be composed of several orders superimposed on each other, and 3—the different blackening effect of the various wavelengths comprising the continuous radiation.

Temperature, as is well known, has a marked effect on the character of slip lines; for example, the amount of shear taking place on slip planes has been shown to be a function of the testing temperature. As pointed out by Dr. Smoluchowski, the temperature of test does not determine the acting slip plane in the case of the nonalkali metals. Whether or not the rationalization based upon the absolute temperature of test holds for the alkali metals should await further studies on carefully documented alkali single crystals of various orientations using different methods to determine the acting slip plane as suggested earlier in the discussion.

—D. L. Averbach and B. E. Warren: Journal of Applied Physics (1949) 20, p. 1068.
—C. S. Barrett: Trans. AIME (1945) 161, p. 15.
—C. S. Barrett: Trans. AIME (1950) 188, p. 123; Journal of Metals (January 1950).
—H. Wilsdorf and D. Kuhlmann-Wilsdorf: Discussion on paper by N. K. Chen and C. H. Mathewson: Structural Studies of Plastic Deformation in Aluminum Single Crystals. Journal of Metals (May 1952); Trans. AIME, p. 528.
—H. Wilsdorf and D. Kuhlmann-Wilsdorf: Naturwissenschaften (1951).
—F. J. Vogel, Jr. and R. M. Brick: Deformation of Ferritic Single Crystals. July 1952. Tech. Report No. 1 to Flight Research Laboratory.
—Ref. 9, Fig. 10.

Plastic Deformation of Magnesium Single Crystals

DISCUSSION, J. E. Burke presiding

G. B. Craig (*University of Toronto, Toronto, Ont., Canada*)—The advent of pyramidal slip at room temperatures in a magnesium crystal (M_{II}) and the very low value reported for the critical shear stress are puzzling. Table II shows the calculated values (approximate) for $\sin\chi\cos\lambda$ in this specimen if all the $\{10\bar{1}1\}$ planes are considered. If S_r is the shear stress resolved in the direction of glide, on the glide plane, and σ_t is the stress operative in yield point tests, then:

$$S_r = \sigma_t \sin\chi\cos\lambda$$

and for (01$\bar{1}$1) the operative slip plane is:

Table II. Values of $\sin\chi\cos\lambda$ for Magnesium Crystal M_{II}

	Pyramidal Planes	χ,	$\sin\chi$	λ,	$\cos\lambda$	$\sin\chi\cos\lambda$
1	(1$\bar{1}$01)	59	0.514	48	0.669	0.344
2	(10$\bar{1}$1)	52	0.788	75	0.292	0.230
3	(0$\bar{1}$11)	76	0.174	14	0.970	0.169*
4	(01$\bar{1}$1)	15	0.259	14	0.970	0.251
5	(10$\bar{1}$1)	65	0.891	75	0.292	0.260
6	(1$\bar{1}$01)	44	0.695	48	0.669	0.465
	(0001)	0		14		0.101

* This is prism slip to be slipped.

$S_r = 325\ (0.169) = 55$ g per sq mm (approximately)

for (1$\bar{1}$01):

$S_r = 325\ (0.465) = 151$ g per sq mm (approximately)

for (0001):

$S_r = 325\ (0.101) = 32.8$ g per sq mm (approximately)

Thus, we see the pyramidal plane in which the minimum shearing component operated. Barrett[1] stated: "Experiments have repeatedly shown that, when there are several crystallographically equivalent slip systems in a crystal, the one having the greatest resolved shear stress will become active. . . ." It does not appear to me that the measurements given are conclusive proof that pyramidal slip operated.

E. C. Burke and **W. R. Hibbard, Jr.** (authors' reply)—Although the low value for the critical resolved shear stress for pyramidal slip may be puzzling, there does not appear to be any basis for questioning the validity of the measurements. Under the influence of constraints, slip systems having decidedly lower shearing components may become operative, e.g., "cross-slip" or the "forced glide" in magnesium reported by Bakarian. Since we believe that pyramidal slip occurred in the specimen because basal slip was inhibited, it is not too surprising to find an operative plane with a lower shear stress.

[1] C. S. Barrett: Structure of Metals (1943) p. 236. New York, McGraw-Hill Book Co.

Delay Time for the Initiation of Slip in Metal Single Crystals

DISCUSSION, D. C. Jillson presiding

C. S. Roberts (*Dow Chemical Co., Midland, Mich.*)—In this study we have seen another example of how modern electronic instrumentation can be of great value to metallurgical research. The authors have shown much ingenuity in their experimental work. However, I wish to point out that anelasticity theory tells us that we must be cautious when we use pulse methods for measurements which are to be correlated with knowledge of static stress-strain behavior.

The basic stress calibrations used by the authors depend on the use of static moduli combined with the pulsed strains. No recognition of a possible modulus defect has been indicated. The general agreement of critical resolved shear stresses may indicate that a

troublesome part of the relaxation spectrum was not involved with some of the materials and temperatures. Nevertheless, I hope that the authors are convinced that no interfering anelastic effects occur.

I. R. Kramer and **R. Maddin** (authors' reply)—The authors wish to thank Dr. Roberts for his comments. The point he raised is an important one, and is one to which we have given considerable thought. The critical resolved shear stress values on both aluminum and α brass obtained by the dynamic methods used in this study are in very close agreement with those obtained by static methods. This would indicate that at least for these metals the effect of the dynamic loading is small. That the anelastic effect is small in the case of α brass does not necessarily follow. This effect should be measured in each case to be certain of the correction which must be made. It should be pointed out, however, that the conclusions arrived at in this paper would not be changed as a result of a correction in the values of the critical resolved shear stress. The curves would be shifted but it is expected that the general shape of the curves would remain the same.

Diffraction Patterns and Crystal Structure of Si_3N_4 and Ge_3N_4

by W. C. Leslie, K. G. Carroll, and R. M. Fisher

DISCUSSION, Robert Maddin presiding

H. F. Beeghly *(Jones and Laughlin Steel Corp., Pittsburgh)*—Since silicon is one of the more commonly used elements in steelmaking, the Si-N system has been the subject of active interest to research workers. With the advent of recently developed experimental techniques, data on the behavior of the system are becoming available. This paper on the structure of silicon nitride represents another valuable addition to this store of knowledge.

We have been most interested in silicon-killed carbon steels and in following the behavior of nitrogen in them during thermal treatment by means of the ester-halogen reagents to which the authors refer. Our results, scheduled to appear soon in *Analytical Chemistry*, indicate that the problem is somewhat more complex than it may initially appear to be. An "acid soluble" Si-N compound can be recovered from silicon-bearing steels heated in the temperature range of approximately 1100° to 1600°F, and the amount recovered from a given specimen varies with the temperature and the time at temperature. However, after holding the specimen in the range of 2200° to 2400°F and quenching in water, the compound can no longer be recovered. In fact, the Si-N data bear a marked similarity to the Al-N data we published in 1949 except that the rate of the Si-N transformations is slower. In higher silicon, aluminum-free steels (1.5 to 3.5 pct Si) we have observed that the nitrogen may be in an "acid insoluble" form. We wonder if the authors have also observed this difference and, if so, whether they have found a difference in the diffraction pattern of the "acid soluble" and the "acid insoluble" form.

Pol Duwez *(California Institute of Technology, Pasadena, Calif.)*—The authors are to be congratulated for their worthwhile study of the structure of silicon and germanium nitrides. A few years ago, we also attempted to work out the crystal structure of silicon nitride from powder patterns. Contrary to what the authors found, it was possible to explain all the reflections with a satisfactory degree of accuracy on the basis of a phenacite type structure (rhombohedral) proposed by Juza and Hahn[4] for germanium nitride. We believe that the evidence presented in the paper in favor of an orthorhombic structure is not sufficient to rule out the alternate rhombohedral symmetry. Single-crystal work will obviously be necessary for a complete structure determination.

W. C. Leslie, K. G. Carroll, and **R. M. Fisher** (authors' reply)—We wish to thank Messrs. Beeghly and Duwez for their interesting comments. In reply to Mr. Beeghly's remarks, we have observed no evidence in our work for the existence of two crystallographic forms of silicon nitride. Identical diffraction patterns were obtained for all steels and heat treatments used in the investigation. It was found that nitrides formed in these silicon steels (0.58 to 3.2 pct Si) partially dissolve in hydrochloric acid and require addition of HF for complete solution. This behavior is believed to be merely an effect of particle size. However, this partial solubility of silicon nitride gives rise to a chemical interference with aluminum nitride when the latter is determined by the method developed by Mr. Beeghly.

Morphology of silicon nitride in a steel is affected by the heat treatment of the steel. The nitride becomes more soluble in the iron matrix as the temperature is raised, but the temperature at which it is completely dissolved will differ with the steel, since it will depend on the concentrations of both silicon and nitrogen. Further comments on this subject appear in the paper by Darken, Smith, and Filer.[5] We agree with Mr. Beeghly's statement that formation of silicon nitride in steel is usually slower than that of aluminum nitride; we would like to add that it is much slower under ordinary conditions.

We agree with Dr. Duwez that a single-crystal study of silicon nitride will be necessary ultimately to settle the question of its structure. Our powder pattern data, however, appear to rule out the rhombohedral structure of Juza and Hahn, as does the data of these authors for Ge_3N_4 when numerical errors are corrected. We would be interested to compare our data with that alluded to by Dr. Duwez for Si_3N_4; in a complicated pattern of this nature, the presence or absence of a few lines would profoundly affect conclusions regarding possible structures. Our pattern for Si_3N_4 is the only one published and, unfortunately, at this time can only be compared with that of the isomorphous compound Ge_3N_4. In our published patterns for the nitrides, all weak lines were carefully checked on several different specimens of the material, to insure that even the faintest diffraction lines were reproducible.

Our main objectives in this work were to establish the existence of silicon nitride in steels and to present a reliable means for its identification. Diffraction patterns of single crystals would be highly desirable, but are not absolutely necessary to the accomplishment of these objectives.

[4] L. S. Darken, R. P. Smith, and E. W. Filer: Solubility of Gaseous Nitrogen in Gamma Iron and the Effect of Alloying Constituents—Aluminum Nitride Precipitation. *Trans.* AIME (1951) **191**, p. 1174; JOURNAL OF METALS, December 1951.

Habit Phenomenon in the Martensitic Transformation

by F. S. Mackin and Morris Cohen

DISCUSSION, V. N. Krivobok presiding

J. S. Bowles and **J. K. Mackenzie** *(Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia)*—The authors are to be congratulated for giving the first direct experimental proof that the observed macroscopic strain accompanying martensite transformations is not necessarily a shear. We

have recently been studying martensite transformations in various systems and a number of general principles have emerged that are relevant to the present paper. This work will be published shortly, but we wish to take this opportunity to comment on the present work in the light of our own conclusions.

We agree with the authors that the factorization of the total strain on transformation into a pair of invariant plane distortions is not unique. This factorization of the total strain is only possible if an invariant direction exists, and is then made unique only by the introduction of two conditions. One condition arises from the observation that twin orientations often coexist in the same martensite plate. In such cases, both twins have suffered the same "first" distortion and it can be shown that the "second" distortions must either be on the twinning plane or in the twinning direction of the final structure. The second alternative appears to be the relevant condition. The other necessary condition is that the "second" distortion be a shear. This follows if the "first" distortion is identified with the macroscopically observed strain, since any dilatational component must be cumulative even in an inhomogeneous distortion.

These two conditions are satisfied by the factorizations which have been suggested for the (225)$_f$ Fe-C and the In-Tl[1] transformations. They also enable satisfactory factorizations to be made for various body-centered cubic $\rightarrow$ hexagonal close-packed transformations such as $\beta_1 \rightarrow \gamma'$ in Cu-Al.[2] The (225)$_f$ Fe-C transformation is degenerate, because pairs of variants of the Kurdjumow-Sachs orientation relationship are twin related and, since the twinning direction is the invariant direction, must have the same habit plane. This, together with the observed coexistence of twins in the plates, implies the unique factorization already given. Alternative factorizations would lead to microstructures in which plates with the same habit plane tilt the surface in opposite senses, as observed in the Cu-Al and In-Tl transformations. For general orientation relationships this degeneracy is not present and both conditions must be used.

The authors' factorization of the (259)$_f$ transformation is in complete agreement with the principles outlined above. Their criterion for the direction of the "second" distortion cannot be successfully applied to other transformations and, although coexisting twins have not yet been reported in Fe-Ni martensite, it is tempting to conclude that our criterion can be applied in all cases. However, we believe that the accuracy of the present results is insufficient for them to constitute a conclusive test of the hypothesis.

In this connection, we wish to bring to the authors' attention the following sources of inaccuracy in the present work.

1—In deriving their final strain matrices the authors have not made use of the most direct and reliable piece of experimental information, namely that the habit plane is the invariant plane. The deviations of the circles from the mean positions of the sets of dots in Fig. 3 indicate clearly that this is a source of error, which will affect the determination of the direction of the "first" distortion.

The authors claim to have verified that the macroscopic distortion is of the invariant-plane type. Their argument is unconvincing because they have assumed this in deriving their strain matrix. Furthermore, their argument is unnecessary because the observed continuity of the transformed plate and matrix, the observed nonrotation of the intersection of the habit plane with the surface and the continuity of scratches crossing the interface establish the nature of the distortion directly.

2—The scatter of the measured habit planes is larger than probable experimental errors. As the authors point out, the habit plane (and the direction of the "first" distortion) will vary with the orientation relationship, and conversely. Thus, unless attention is confined to data with the same habit plane (within the experimental error), there will be unknown errors in the estimation of the direction of the "first" distortion and in the elements of the "second" distortion. In order to compare the various habit planes all the data should be reduced to a single variant.

3—In deriving the strain matrices from the experimental data, the authors have assumed that $t_{xz} = t_{yz} = 0$ exactly, and hence that the direction of the "first" distortion lies in (111)$_f$. From their estimate of the experimental error (± 0.01) in measuring t_{xz}, t_{yz} it follows that the direction of the "first" distortion can be as much as 5° out of the (111)$_f$ plane.

If the (111)$_f$ plane is unrotated, the authors are justified in neglecting the errors in t_{xz} and t_{yz}. However, Greninger and Troiano[3] have already shown that the (111)$_f$ plane is rotated through about 1° in the (259)$_f$ Fe-Ni-C transformation. It can be shown that even if the (111)$_f$ plane is rotated by only ½° the unrotated plane containing the two directions of atom motion may be as much as 15° from the (111)$_f$ plane. Thus it is very dangerous to accept observed zero rotations at their face value.

4—When the data given for the variants shown in Fig. 2 are referred to a single variant it is found that, with the exception of the [111]$_f$ direction, all the directions studied lie in the same (111)$_f$ plane. Since the direction of atom motion lies close to this same (111)$_f$ plane, and since no extensions could be measured, it follows that only the projection of the direction of atom motion on the (111)$_f$ plane can be satisfactorily estimated. Had other variants, or other directions, been considered it may have been possible to rectify this.

5—The second distortion determined by the authors in Appendix IV is not, as claimed, close to an invariant plane strain, since, in the axes of the matrix B, the points at 1, 0, 0 and 0, 0, 1 move in quite different directions. While the authors are justified in restoring the diagonal elements of their strain matrix for the "first" distortion as in Appendix III, they are certainly not justified in doing the same for the second matrix because it is uniquely determined by the "first" distortion and the known total strain. Because of the probable inaccuracies in determining the strain matrix of the "first" distortion, and the uncertainty in the orientation relationship, it is not surprising that the authors' experimental evidence does not establish conclusively that the second distortion is a shear in the twinning direction.

6—The habit planes a-f in Table I are incorrectly indexed; the indices given in Figs. 2 and 3 are correct. We also wish to point out that the poles labeled (295)$_f$ in these figures are incorrectly plotted; the directions [295]$_f$, [925]$_f$, and [110]$_f$ are coplanar.

We wish now to comment on the authors' views concerning the physical mechanism of the production of martensite plates.

The factorization of the total strain of the transformation into two invariant plane strains is a means of describing consistently "what has happened" rather than "how it happened." To determine the particular physical processes involved it is necessary to have more information.

Following Greninger and Troiano, and Bowles, the authors have assumed that the observed macroscopic distortion occurs first. The argument used by the authors to establish the order in which the hypothetical component distortions occur is therefore circular. In any case, it is invalid since each distortion prescribes a vector displacement of each atom and the resultant displacement is independent of the order in which they are combined. The strain matrices do not commute because interchanging their order does not simply interchange the order of these vector displacements. It should be pointed out that in Appendix V the matrices A and B are not referred to the same axes.

Every possible mode of transformation involves the production of a certain volume of material with intermediate structures. Since the activation energy asso-

Fig. 17 (left)—Laminated martensite formed in an electropolished Fe-Ni-C specimen. Unetched. X150. Area reduced approximately 50 pct for reproduction.

Fig. 18 (right)—Same area as in Fig. 17 after cooling to a lower temperature. X150. Area reduced approximately 50 pct for reproduction.

ciated with a mode of transformation increases with this volume, it is clear that the mode which makes this volume as small as possible will be preferred. As the authors have pointed out, a mode of transformation in which the strain is propagated from a localized nucleus will require a smaller volume in an intermediate state than one in which all atoms in the plate move simultaneously. They envisage movement of atoms within a localized strain gradient having a volume proportional to the final thickness of the plate. However, the volume of material in an intermediate state can be reduced still further if the transformation occurs by the rapid motion of a strain gradient which is localized within atomic distances in at least two (or perhaps three) of its dimensions. The final decision between these possibilities awaits detailed comparisons of their activation energies with the free energy available for the transformation, and of the predicted rates of formation of plates with those experimentally observed.

There is some experimental evidence indicating which of the above possibilities is most likely. In the Au-Cd[4] and In-Tl transformations thin plates are produced very rapidly and these then broaden at a slower rate. This suggests that at least in these transformations the propagating strain gradient is localized about a line (or a point) which moves rapidly in the habit plane. The strain gradient would be localized both in (at least) one direction parallel to the habit plane, as suggested by the authors, and also in the direction normal to the habit plane.

Very similar behavior is observed for the (259)$_\gamma$ transformation in cast Fe-Ni-C specimens containing 19.4 to 21.0 pct Ni and 0.8 to 1.0 pct C on quenching or slow cooling (1° per min) to liquid nitrogen temperatures. As shown in Figs. 17 and 18, the martensite plates first form as packets of very thin lamellae which on further cooling broaden (whether by growth or the formation of new lamellae is unknown) and eventually build up a complete "normal" plate. The conditions required to produce this "laminated" martensite have not yet been clarified. This mode of transformation is not connected with the state of the surface (mechanical or electrolytic polishing) or with the state of deformation.

C. S. Roberts (*Dow Chemical Co., Midland, Mich.*)—This careful piece of work shows that, as is often the case in transformation studies, if one is willing patiently and carefully to carry through analyses of considerable complexity, the overall picture of a phenomenon becomes simpler and more general. It appears that the authors have made a conscious effort to harmonize their conclusions with all the pertinent and reliable observations.

As a result of the "least-resistance" reaction path concept, the authors believe that the change of habit in the Fe-C system at about 1.4 pct C implies the existence of two alternate reaction paths. I have wondered why as carbon atoms are continuously added to the lattice in this region it becomes easier to initiate the first strain on (259)$_\gamma$ rather than on (225)$_\gamma$. Because of the relative scarcity of carbon atoms in the lattice even at the highest end of the solubility range it seems likely that this effect results indirectly from their influence on the average interatomic distance for iron atoms. To my knowledge no good structure studies have been made in the very high carbon austenite range. Perhaps some changes occur in the positioning of the carbon atoms, either with respect to type of interstices or randomness or both.

E. S. Machlin and **Morris Cohen** (authors' reply)—The penetrating discussion of Drs. Bowles and Mackenzie constitutes a valuable supplement to this paper. Their thorough analysis has brought to light some inadvertent errors which the authors will rectify in the course of this reply.

The authors agree that their criterion for the second strain (p. 1023 of the paper) is not a general one. The alternate criterion proposed by Drs. Bowles and Mackenzie is undoubtedly more satisfactory, considering its applicability to several systems. Their concept that the second strain should be a shear on the twinning plane or in the twinning direction of the final structure is certainly in harmony with the ideas expressed in this paper.

The following remarks are in specific reply to the itemized comments of the discussers:

1—We did not take it for granted that the habit plane is parallel to the invariant plane because we wanted to learn if this parallelism really exists. To verify the occurrence of an invariant-plane strain, the procedure was to set up a strain matrix involving an invariant-plane motion in general form, and then show that the observed displacements are not only consistent with this matrix but yield a definite solution for the orientation and direction of motion of the invariant plane. This type of demonstration is analogous in principle to assuming that a certain form of equation relates certain variables; then experimental data is used to justify the equation and establish its constants. For example, the diffusion equation $D = D_0 e^{-Q/RT}$ is employed in just this sense for the determination of the frequency factor D_0 and the activation energy Q when the diffusion coefficient D is known as a function of temperature T. The prevalent continuity of scratches across the austenite-martensite interfaces tends to substantiate the occurrence of an invariant-plane strain, but we did not feel warranted in accepting this observation alone as proof. In fact, continuity of scratches was not always assured.

2—The scatter of the habit-plane determinations is beyond the experimental error and may be inherent in these systems where considerable plastic deformation attends the transformation. There is no point in reducing the data to a single variant as this would destroy one of the main features of the investigation: namely, the direction correlation of a specific habit permutation with a specific transformation strain (T matrix).

3—The assumption that the (111)$_\gamma$ plane does not rotate ($t_{zz} = 0$) introduces relatively little error. If t_{zz} is taken equal to 0.01 (the estimated uncertainty in this measurement), the invariant plane of the first strain differs from that given in the paper by less than 5°. Thus, the correlation found between a specific experimental habit plane and the invariant plane of the corresponding transformation strain is good within 5°.

4—Other variants had been checked and no contradiction was found with the assumption that, within the experimental error, the direction of atom motion lies in a (111)$_\gamma$ plane.

5—This point of the discussers is well taken. The observations and calculations are such as to cause a comparatively large uncertainty in the evaluation of the second strain. Nevertheless, the elements reported

for the second strain may be considered to be an average result, having reasonable significance. When the stereographic method was applied, these elements were yielded as solutions for the second strain using the measured first strain and the Greninger-Troiano orientation relationships as the known parameters.

6—The habit-plane designations in Table I are incorrect, as stated by Drs. Bowles and Mackenzie. The last column of Table I should read: *a* — (592)$_\gamma$, *c* — (259)$_\gamma$, *e* — (925)$_\gamma$, *b* — (295)$_\gamma$, *d* — (529)$_\gamma$, *f* — (952)$_\gamma$. Also the (295)$_\gamma$ pole in Figs. 2 and 3 should have been plotted just to the right of the vertical line instead of just to the left.

The discussers are also correct in pointing out that the commutative test used in Appendix V is not valid. Hence, the principal basis for assuming the given order of strains is that, if the unobserved strain is to be taken as a shear in the twinning direction of the final structure, the observed strain might well be expected to occur first in order to set up the conditions for the "second" strain. This sequence is in line with the conclusions of Greninger and Troiano[5] and of Bowles[2] as well as with the factorization criterion of the discussers.

The formation of martensite in clusters of thin *lenticular is a most interesting phenomenon.* It has also been found recently by Reynolds and Bever in a Cu-Zn alloy when the transformation is induced by stress.[7] It is hoped that Drs. Bowles and Mackenzie will continue their work on the Fe-C-Ni alloys to clarify this complex mode of the martensitic transformation.

Dr. Roberts has inquired about the two alternate reaction paths leading to the [225] and [259] habits. While the minimum activation energy along competitive paths might well depend on the carbon content, an *a priori* explanation is not available at the present time. It is possible, as Dr. Roberts suggests, that the exact positioning of the carbon atoms in the austenite lattice may undergo a change with increasing carbon content. Petch's investigation[8] of the location of the carbon atoms in austenite was conducted on an Fe-C-Mn alloy containing 1.3 pct C and 13 pct Mn. The corresponding habit is not known. To study the effect of carbon content on the carbon positioning would probably require the introduction of an alloying element like nickel or manganese in order to provide completely austenitic structures at room temperature.

[5] J. S. Bowles, C. S. Barrett, and L. Guttman: Trans. AIME (1950) 188, p. 1478; Journal of Metals (December 1950).
[6] A. B. Greninger: Trans. AIME (1939) 133, p. 264.
[7] L. C. Chang and T. A. Read: Trans. AIME (1951) 191, p. 47; Journal of Metals (January 1951).
[8] J. E. Reynolds, Jr. and M. B. Bever: On the Reversal of the Strain-Induced Martensite Transformation in the Cu-Zn System; Journal of Metals (October 1952); Trans. AIME, p. 1069.
[9] Petch: Journal Iron and Steel Inst. (1942) 145, p. 111.

Isothermal Martensite Formation in an Iron-Chromium-Nickel Alloy

DISCUSSION, V. N. Krivobok presiding

R. C. Shnay (*Dept. of Mines and Technical Surveys, Ottawa, Ont., Canada*)—The authors are to be congratulated on an interesting and informative paper. However, several questions arise when the isothermal formation of martensite is considered in relation to the formation of bainite at temperatures near the M_s point. The reactions in an alloy and in a plain carbon steel would appear to be comparable; and in the course of a recent investigation of the austenite-bainite transformation in a plain carbon steel,[1] the writer has obtained data at temperatures above and below the M_s point. These data are in some respects similar to those of the authors and a comparison would seem justified.

The steel used in this investigation had the nominal composition: C, 0.80 pct, Mn, 0.20, and Si, 0.20. The course of the transformation was followed by the use of a magnetic balance. The magnetic moment of the specimen as determined by this instrument is directly proportional to the percentage of the total volume of the specimen which has transformed to bainite.

All specimens were austenitized at 1850 F for 4 hr, quenched to the transformation temperature, and quickly transferred to the magnetic balance. Readings were taken at regular intervals until the transformation had stopped. A typical transformation curve is shown in Fig. 9.

The preliminary curve preceding the S-shaped curve

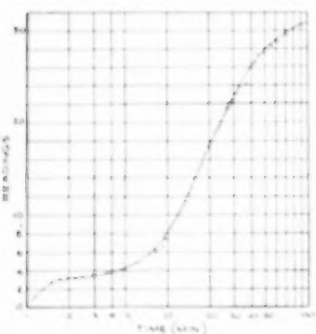
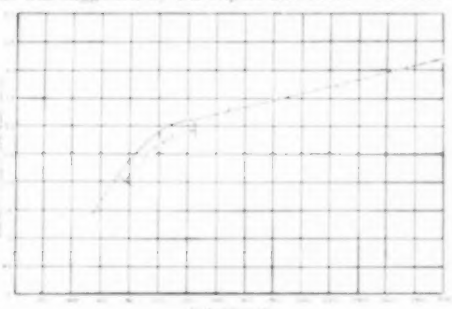


Fig. 9 (left)—Transformation of austenite to bainite at 460 F

Fig. 10 (right)—Preliminary or first stage of bainite formation at 460 F

Fig. 11—Bainite plates formed during the preliminary stage at 480 F. Matrix is martensite formed on quenching to room temperature. Etchant, 2 pct nital. X1000.

was found at all temperatures above the M_s to around 600 F. Both the extent of this preliminary curve and the time interval between it and the S-shaped curve were found to decrease with increasing temperature as was suggested by Davenport and Bain.[6] Therefore,



it is difficult to say with certainty whether the preliminary curve disappears at higher temperatures or is merely not detectable with the magnetic balance used in this investigation. The shape of this part of the bainite transformation curve is illustrated on an enlarged scale in Fig. 10.

The microstructure of a specimen allowed to transform for only 2 min at 480°F, Fig. 11, shows that some of the new phase is formed as dark-etching blade-shaped particles during the preliminary stage. Microscopic inspection of specimens allowed to transform for longer periods showed a gradual growth of the particles formed during the first stage of the transformation.

The writer would be interested in the authors' opinion on whether this preliminary stage of bainite formation is the same as, or in any way related to, the isothermal formation of martensite above the true M_s, which they describe in their papers.

S. A. Kulin and **G. R. Speich** (authors' reply)—The authors wish to thank Mr. Shnay for his interesting discussion. It is quite possible that the initial portion of the curves shown in Fig. 9 may be due to the isothermal formation of martensite above the M_s temperature. However, some questions are raised concerning Mr. Shnay's work:

1—Due to the unusually long austenitizing time (4 hr at 1850°F), what precautions were taken to prevent decarburization? If decarburization did take place, the decarburization layer would transform before the matrix. This might give an alternate explanation for the initial portion of the curve in Fig. 9.

2—The curve in Fig. 10 does not extrapolate to the origin. If the initial portion of the curve is due to the isothermal formation of martensite, then no incubation period should be present.

[8] R. C. Shnay: A Magnetometric Investigation of the Austenite-Bainite Transformation. M. A. Sc. Thesis, University of British Columbia, 1951.

[9] E. S. Davenport and E. C. Bain: The Transformation of Austenite at Constant Subcritical Temperatures. *Trans.* AIME (1930) 90, p. 117.

Isothermal Transformation Characteristics of an Iron-Chromium Alloy of Titanium

by Charles W. Phillips and Donald N. Frey

DISCUSSION, V. N. Krivobok presiding

W. Rostoker (*Armour Research Foundation, Chicago*)—As I understand the text of this paper, the M_s and M_f temperatures were determined from the hardnesses of samples which had been step-quenched, the intermediate temperature being lowered with successive samples. Since according to the simple behavior of a martensitic reaction, the amount of martensite is dependent only on the lowest temperature of quench, i.e., room temperature, I do not see how the hardness curve of Fig. 18 can be reasonably related to M_s and M_f temperatures. Obviously, however, the authors have a hardness anomaly. May I suggest that the origin is related to stabilization of the β phase? In a recent paper,[1] we pointed out that such an effect was operative in Ti-Mo alloys when step-quenching techniques were adopted. For instance, specimens of a 7 pct Mo alloy quenched to 1020°F and held for 1 and 15 sec, respectively, prior to water quenching showed in the former case, profuse α' and in the latter case, only small amounts of that phase in a matrix of apparently retained β. However, it was noted that this retained β was anomolously harder than β normally retained by quenching at higher alloy contents and also harder than the normal as-quenched structure. It must therefore be inferred that the stabilization process imparts some undetermined change. We, and others who have noted this effect, have chosen to designate this unusually hard β as β'. This β' has also been noted in as-quenched Ti-Cr and Ti-Fe alloys. With increasing chromium or iron contents, the as-quenched hardness increases and the amount of α' decreases. The peak in the as-quenched hardness curve occurs in alloys which show no α'. With further additions of alloy content, the as-quenched hardness drops.

The writer feels that the type II reaction differs from the type I reaction only in degree. The lattice parameter evidence presented in the paper and our own experience would indicate that the structure in Fig. 7 is merely an (α + β) phase mixture of extreme fineness. This is the type of structure which may be expected at or below the "nose" of the C curve. With successively longer holding times the plates of α grow both in length and thickness as the β phase is further depleted of titanium.

It is by no means improbable that eutectoidal rejection of TiCr$_2$ or TiFe or both can occur at 1000°F even in quite a short time. The writer does not suggest that the structures in Figs. 11 to 15 are necessarily eutectoid but that it would be fallacious to dismiss the possibility. Recent work at the Armour Research Foundation places the ternary eutectoid at about 1000°F. It is also known that gaseous contaminants raise the eutectoid temperatures. The absence of TiCr$_2$ or TiFe lines in X-ray diffraction patterns should not be taken as evidence of their absence in the structures as their amount at best could only be very small. We have found that TiCr$_2$ lines can only be reasonably detected in alloys containing at least 5 pct Cr and then only toward the completion of the eutectoid reaction. The occurrence of eutectoid in 1 hr is not unreasonable in view of the oxygen plus nitrogen content. We have found these elements to have a tremendous accelerating effect on reaction rates. The writer would be surprised if the soaking treatment in air at 1800°F for 1 hr on 0.11 in. thick slugs did not increase the oxygen and nitrogen contents. It might also be mentioned that a similar structure was noted in a 5 pct Cu-Ti alloy but after further careful surface preparation, the irregular dark etching plates disappeared.

Finally, the writer would question the advisability of introducing new designations of reaction types without more substantial proof of their singularity.

C. W. Phillips and **D. N. Frey** (authors' reply)—Dr. Rostoker's initial statements indicate that we have not presented the rationale of the determination of the M_s temperature with sufficient clarity. On step quenching to successively lower temperatures above the M_s the final product at room temperature (assuming no nucleation and growth decomposition of β) will be largely or completely martensite, and the hardness will be a maximum. On step quenching to below the M_s temperature the martensite which is formed tends to decompose into α and β, or ω and another phase, of equilibrium compositions by diffusion. The higher the temperature (below the M_s) the greater the rate of decomposition and therefore the softer the structure at a given short time interval in the step quenching process. This conforms to the left hand portion of Fig. 18 up to about 1000°F.

In the M_s-M_f range the hardness will be a function of the proportions of martensite formed on the second quench (from retained β) and the proportion of decomposed martensite due to holding after the first quench.

The increase in hardness above 1200°F is thus explained by the increasing amounts of martensite formed on the second quench. The temperature at which the sharp inflection in the curve is observed is then taken as the M_s temperature.

In view of the fact that a hardness increase accompanied the process referred to as β stabilization in the reference cited, which is directly opposite to the pres-

cutly observed hardness trends on short time isothermal holding, stabilization does not seem to be a reasonable explanation of the latter.

The structures of Figs. 7 and 10 are, as Dr. Rostoker suggests, α and β—formed by the process just mentioned—and the term "acicular α" which we have considered as synonymous with α perhaps should be modified with the adjective "tempered," as in the case of the others.

The lack of inflections or discontinuities in the β lattice parameter curves is to be expected, since variations in composition are a result of alloy component diffusion and therefore would alter the parameter continuously with time and temperature, whether the initial structure was β of the total alloy composition, or supersaturated α formed on passing through the M_s temperature, the proportion of the latter phase also being a continuous function (although not linear) with temperature.

The authors agree that the dark etching constituent could be the result of the eutectoid reaction, and that the absence of X-ray lines attributable to the TiCr$_2$ and TiFe phases does not eliminate the possibility of their presence. We also agree that the oxygen introduced by solution treatment in air could affect the reaction rates.

The suggestion that the structure of Figs. 11 to 15 is a sample preparation artifact is unacceptable. No differences were noted between samples mechanically and electrolytically polished. A structure very similar to this one in question is presented by H. M. Worner[9] of an aged titanium-5.9 pct Fe binary alloy.

The reaction designations were employed merely for the sake of brevity.

D. J. DeLasaux, M. Hansen, R. E. Riley, and W. Rostoker: Time-Temperature-Transformation Characteristics of Titanium-Molybdenum Alloys. Journal of Metals (March 1952), Trans. AIME, p. 265.

[9] H. M. Worner: Journal Inst. Metals (January 1952) **80**, p. 213, Fig. 4.

Work Hardening-Reannealing Cycle of Pure Silver

by Wayne Rohrbach and Walter Crafts

DISCUSSION, V. N. Krivobok presiding

J. L. Christie (*Handy and Harman, Bridgeport, Conn.*)—The authors' test results show hardly any evidence of self-annealing during the actual wire drawing. In Fig. 1 there is only a suggestion of changes in slope of the curves beyond 80 pct reduction. In actual practice it is necessary to make sure that reductions made in tandem or in rapid succession do not heat the silver hot enough to cause self-annealing if maximum hardness is to be obtained.

Kinetics and Orientation Relationships of Secondary Recrystallization in Silver

by F. D. Rosi, B. H. Alexander, and C. A. Dube

DISCUSSION, V. N. Krivobok presiding

F. H. Wilson (*American Brass Co., Waterbury, Conn.*)—The type of grain coarsening, to which the authors refer with respect to the observations of Cook and Richards on copper, occurs at reductions of 50 to 60 pct. The large grains grow in a matrix which has only a partially developed preferred orientation and the orientations are distinctly different from the ones found as a result of secondary recrystallization in cubically aligned copper. Since the silver used by the authors was rolled only 50 pct, their story would be more complete if they would demonstrate by a pole figure that the matrix in which their large grains are growing is indeed a well-developed (113) [112] texture.

F. D. Rosi, B. H. Alexander, and **C. A. Dube** (authors' reply)—In anticipation of the suggestion by Dr. Wilson, we have done additional work toward determining the texture of the primary recrystallization structure. Although a complete pole figure is not available at the present time, the results obtained thus far by X-ray analysis appears to establish the presence of a rather strong (113) [211] texture in the recrystallized (400° to 500°C) strips.

Although the material was given a final reduction of only 50 pct, it must be remembered that there were several prior reductions followed by low process anneals. It has been shown[7] that such a rolling schedule can result in a high degree of preferredness. To substantiate this, the (110) pole figure for the cold-rolled material is shown in Fig. 13.

S. F. Reiter (*General Electric Research Laboratory, Schenectady*)—Figs. 1 and 6 of this very interesting paper indicate that the coarse grains produced in secondary recrystallization are rather uniformly distributed over the sheet. I would like to know if the authors have data depicting the nucleation rate for these crystals, and the rate at which secondary grains consume the primary recrystallized structure. It would be interesting to see if a nucleation and growth analysis could predict the progress of secondary recrystallization.

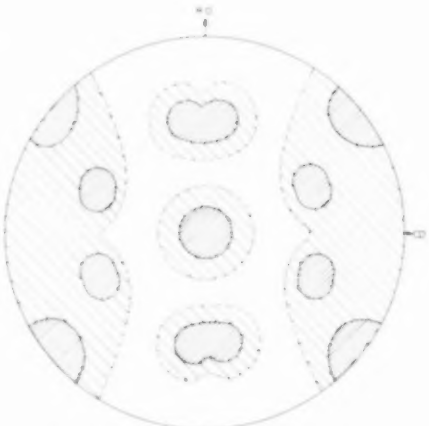


Fig. 13—(110) pole figure for cold-rolled silver.

F. D. Rosi, B. H. Alexander, and **C. A. Dube**—No work was done toward determining the nucleation rate for the secondary transformation, since it was believed that the end result of such a tedious analysis did not justify the additional time and effort. For example, I seriously doubt whether the results of a nucleation analysis would tell us any more regarding the origin of nuclei for the secondary transformation than could be inferred from the growth velocity measurements.

[7] F. W. Pulmes and C. S. Smith: Trans. AIME (1942) **147**, p. 164.

by A. N. Holden

DISCUSSION, V. N. Krivobok presiding

C. S. Roberts *(Dow Chemical Co., Midland, Mich.)*—The author's ingenious modification of Cottrell's original dislocation mechanism has interested me very much. I am sure that this classical old problem merits such fresh and general approaches as this one. The author points out Cottrell's inability to eliminate the theoretical prediction of some homogeneous flow prior to the yield point and described this as inconsistent with experiment. In an experimental study carried out at MIT[1] such prior flow was found in well-annealed polycrystalline specimens. Special care in alignment and a special strain measuring technique which gave the plastic strain with an accuracy of $\pm 4 \times 10^{-6}$ were used. Strains below the yield point of the order of 50×10^{-6} were observed for plain carbon steels in conditions which led to observation of yield points. The smoothness of the stress-plastic strain curves indicated homogeneous flow, but no direct evidence of homogeneity was obtained. Of possible theoretical interest is the discovery in the same study that, up to an upper limit of grain size, lower yield points in plain carbon steels and commercially pure irons were a linear function of the logarithm of the mean path in the massive ferrite.

I appreciate the author's economy of experimental effort as manifested by his series of "critical experiments." However, I question whether his experiment using previous strain by rolling a single crystal was truly critical. In general, I would expect the rolling to cause slip on planes operative later in tension. Perhaps with great care previous tension along an axis could be used where it would be certain that common slip planes would not result in the later test.

Finally, I would appreciate the author's comment on the apparently finite stress level shown at zero strain in Fig. 6.

H. W. Paxton *(University of Birmingham, Birmingham, England)*—I should like to describe some experiments on the yield phenomenon in single crystals of iron which have been carried out in the University of Birmingham during the last four years under the direction of Professor A. H. Cottrell. The trend of the experiments shows unquestionably that as the testing technique is improved, so also is the load drop between upper and lower yield stresses increased.

The crystals used were in the form of 2 mm wire and were grown by the conventional strain annealing of decarburized material. Crystals were grown from Armco iron and from two different mild steels. After growing, they were carburized at 700°C in n-heptane vapor diluted with dry hydrogen. The perfection of the crystals was checked by sharpness of back-reflection Laue spots, and by Guinier's[2] focusing Laue technique. Sharp single spots were observed.

In preliminary experiments,[3] Churchman was able to obtain a horizontal portion on the stress strain curve at room temperature corresponding to a lower yield point extension of about 0.25 pct. The technique used was to solder the specimens into coaxial mild steel endpieces using a suitable mounting jig. These were attached to the straining points via Bowden cable and ball seatings which permitted self-aligning under load. A "hard" testing machine was used which gave large load drops for small extensions of the specimen.

By testing at a lower temperature (−77°C) using the same mounting conditions, clear upper yield points (load drops of order 20 pct of upper yield stress) were observed in unstrained crystals. This is presumably because the upper yield stress (as realized by this mounting technique) rises more steeply with falling temperature than the lower yield stress.

Recently, by further increasing the care taken in aligning the specimens in the endpieces, I have been able to obtain upper and lower yield stresses in crystals tested at room temperature and at 70°C. The maximum load drop is about 8 pct of the upper yield stress and corresponds to a sudden elongation of about 0.003 cm in a 3 to 4 cm gage length. In these experiments, nine out of ten specimens showed a load drop (Table II) during the first straining; the remainder showed a flat horizontal portion of the stress strain curve at the yield point.

Table II. Yield Stresses and Yield Points

	Specimen No.	Upper Yield Stress, Kg per Sq Mm	Lower Yield Stress, Kg per Sq Mm	Lower Yield Point Extension, Pct
Mild Steel	VH 4	7.50	7.43	0.3
	VH 8*	7.48	7.19	0.6
	PXG 9	7.61	6.62	0.5
	PXG 10*	8.09	7.32	1.0
	PXG 11* **	6.38	6.15	0.25
	PXG 12	6.15	6.11	0.2
	PXG 23†	6.21	5.76	0.35
Armco Iron	ATC 110	5.40	5.05	0.3
	ATC 112	5.71	5.35	0.3
	ATC 113	5.59	5.22	0.25

* Two or three crystals in series in gage length.
** Rate of testing 6 times slower than PXG 10.
† Tested at 70°C.

Because of these results, we are inclined to think that: 1—virgin unstrained crystals containing carbon or nitrogen are capable of showing the yield phenomenon, 2—that when this capability is not realized in practice, it is because of stress concentrations developed through imperfections in the testing technique, and 3—the upper stress could be raised considerably above its present highest value by further refinements in technique.

A. N. Holden (author's reply)—The author is grateful for the discussions to this paper by C. S. Roberts and H. W. Paxton.

The observation described by Mr. Roberts that small amounts of plastic flow may occur prior to the yield point itself is interesting but not contradictory to a collision mechanism. If the deformation is slow enough so that the carbon atmospheres can move with the dislocations, creep can occur at stresses below the yield point. The load application must be reasonably slow, however, for this to happen. Perhaps such diffusion controlled creep would be detected with the slow stepwise loading employed in Robert's work.

The experiment on rolled single crystals is as Mr. Roberts suggests not critical to the collision mechanism. It was included in the paper as an interesting side experiment that seemed to have a ready explanation if it was assumed that the planes operative in rolling and tension were not identical. Another indication that deformation planes are not completely identical in the two cases is found in the fact that a rolled sheet crystal changes little in width, while a tensile deformed crystal usually changes in both width and thickness.

The initial stress in Fig. 6 is shown as a finite stress because it was finite, and the value of stress reflects the weight of the lower grip prior to any strain measurement.

I am happy to agree with Mr. Paxton in that since this paper was written I have been able to obtain sharp initial yield points in single crystals of iron. I shall have to disagree however with his view that it is simply a matter of improving alignment. I have devoted much fruitless time and effort in perfecting alignment, and I have concluded that when a sharp yield point exists even moderate to poor testing techniques will fail to obliterate the effect.

In general our experience indicates that there are three directions in which it is possible to proceed to sharpen the initial yielding effect in single crystals:

1—The testing temperature may be lowered from room temperature.

2—The specimen may be pre-stressed. The information on pre-stressing has been published.[9] Briefly, if an apparent elastic stress is applied to a crystal and if that stress is maintained for 1 hr or so before completing the stress-strain curve, a pronounced drop in load may be obtained in a crystal that otherwise might have only a flat horizontal initial yield.

3—The dimension of the specimen cross section most closely coinciding with the slip direction may be increased. As a consequence of the size effect described in this paper, many additional tests have confirmed that increasing the total available slip path will enhance the yield point. I hope the results of these additional tests may be published in the near future.

[9] C. S. Roberts, B. C. Carruthers, and B. L. Averbach: The Initiation of Plastic Strain in Plain Carbon Steels. *Trans.* A.S.M., (1952) 44.

[10] A. Guinier and J. Tennevin: *Acta Cryst.* (1949) 2, p. 133.

[11] A. T. Churchman and A. H. Cottrell: *Nature* (1951) 167, p. 843.

[12] A. N. Holden: *Journal of Applied Physics* (July 1952) 23, p. 789.

Effect of Prior Strain at Low Temperatures on the Properties Of Some Close-Packed Metals at Room Temperature

by W. C. Ellis and E. S. Greiner

DISCUSSION, V. N. Krivobok presiding

I. Broom (*University of Birmingham, Birmingham, England*)—The authors' results are valuable in showing the kind of properties which could be expected if subzero deformation were carried out as part of a commercial schedule. The effect of prior strain at low temperatures on mechanical properties is of obvious commercial interest, as suggested by Beilby.[1] In drawing copper wires approximately 5 pct at −80°C and 16°C after a previous reduction of approximately 47 pct at room temperature, he found an improvement of 6.6 pct in the ultimate tensile strength (measured at room temperature) of the wire deformed partly at −80°C compared with that of the wire deformed wholly at room temperature. It is likely that normal working at room temperature, followed by a final deformation at a lower temperature is likely to have important practical advantages over a procedure involving deformation carried out entirely at the lower temperature, even though the improvement in mechanical properties may be slightly less.

It would be interesting to know the times which elapsed between wire drawing and measurement of resistance in view of the authors' statement that: "It is reasonably certain that . . . there has been at most only an inappreciably small recovery at room temperature after drawing and prior to measurement." It has long been known[2] that recovery of resistivity at room temperature can occur even after deformation at room temperature and recent work[3,4] has shown that rapid recovery at room temperature occurs after deformation at low (−183°C) temperatures. This work has aroused much interest in view of the interpretation that a part of the increase in resistivity is due to the presence of vacant lattice sites generated in the deformation process. It is the movement of these vacancies which is thought to give rise to rapid recovery, and this provides a reasonable amplification of the authors' view that "recovery is described as involving single atoms or small groups."

Table III. Fractional Increases in Resistivity Relative to Resistivity at 20°C

Metal	Temperature of Deformation and Measurement, °C	Deformation, Reduction in Area, Pct	Fractional Increase in Resistivity
Copper	−183	90	0.059
	20	90	0.065
Nickel	−183	90	0.075
	20	90	0.080

Experiments have been carried out[5] in which wires have been drawn at subzero temperatures and their resistances measured before removal from the low temperature bath. Special arrangements were made to allow continued drawing without allowing the temperature of the wire to rise. Some typical results for copper and nickel are given in Table III. These values are all appreciably higher than those given by the authors for wires whose resistances had been measured at 20°C after low temperature deformation and serve to emphasize that in work of this kind it is absolutely necessary to take account of recovery.

Finally, the authors in asserting that: "electrical conductivity is a sensitive indicator of the state of strain in a material," imply, by the references given, that their term "state of strain" corresponds to density of dislocations. However, electrical conductivity is dependent not simply upon the density of dislocations but also upon their arrangement, and upon the effect of other lattice disturbances such as vacancies and stacking faults. It is because of its dependence upon so many complex factors that conductivity is an unsuitable property for the indication of mechanical properties, as shown by the authors' results.

W. C. Ellis and **E. S. Greiner** (authors' reply)—The measurements of resistance reported in the paper were never made short of one day after completion of drawing the wire, and often two or three days may have elapsed. However, there is another aspect of the procedure in drawing, which may be of as great importance, and which was not emphasized in the paper in the interest of brevity. During the drawing, the wires were warmed to room temperature between each pass through the dies; the wires were refrigerated only during the actual time they were undergoing deformation, and for the larger reductions, there may have been as many as ten cycles of cooling and heating. We are quite ready to agree that, in such a preparation of the specimens, a strain, relaxing rapidly at low temperatures, is not reflected in our measurements. For example, in our measurements we would not find evidence for the strain associated with the relaxation at low temperatures so nicely demonstrated in two brief papers by Druyvesteyn[6] and Manintveld.[7] The relaxation at −100° to −50°C, and the one near room temperature had already occurred in our specimens before measurement. In fact they would have likely occurred in the interval between each drawing pass. Measurements at low temperatures are valuable, as demonstrated by Druyvesteyn and Manintveld, in revealing relaxation processes but they are hardly a part of the comparison of the effects residual at room temperature in specimens deformed at room temperature and at lower temperatures, the subject of this paper.

It is probably worthwhile to reiterate the main the-

oretical point of the paper, which is to suggest the importance of considering recovery as going on concomitantly with hardening during plastic flow; the recovery contribution decreases as the temperature of deformation is lowered. The larger increase in resistivity resulting from deformation at lower temperatures is interpreted to be due to a higher state of residual strain, a net effect of less recovery during the deformation.

We welcome the data included in the valuable discussion by Mr. Broom; particularly in that, if we interpret the data correctly, it confirms the findings of our paper. Mr. Broom found a greater fractional increase in resistivity, the lower the temperature of deformation when the measurements were made at low temperature, just as we did in our studies when the measurements were made at room temperature. We anticipate reading the full report of his work when it is published.

We feel impelled to reassert that electrical conductivity is a sensitive indicator of the state of strain in a metal. It was unfortunate however that Mr. Broom inferred that the authors believe the only source of electron scattering is in the densities of the dislocations. There seems to be reasonably good grounds for thinking that almost all of the imperfections and interactions among imperfections, in crystals may[5] be sources of added electrical resistivity. It could be wished that, after selecting one property for measurement, it could unequivocably be said that the changes in its value were due to one mechanism or one construct, and one alone. We had no such ambitious objectives in the work reported in this paper. Such decisive experiments are not often available.

[5] G. Beuby: Aggregation and Flow of Solids (1921) p. 152. London: Macmillan Co.
[6] H. Tomlinson: Phil. Trans. Royal Soc. (1883) 174, p. 110.
[7] J. Mostowski and W. H. Astbr: Nature (1950) 686, p. 166.
[8] T. H. Blewitt, W. Taylor, and R. R. Coltman: Physical Review (1951) 87, p. 769.
[9] M. J. Druyvesteyn and J. A. Manintveld: Nature (1951) 168, p. 688.
[10] J. A. Manintveld: Nature (1952) 169, p. 623.
[11] T. Broom: Proc. Phys. Soc. (1952) 65B.

Analytical Representation of Certain Phase Boundaries

by W. Rostoker

DISCUSSION, F. N. Rhines presiding

L. Seigle (*Sylvania Electric Products Inc., Bayside, N. Y.*)—The value for the heat of transition of α to γ iron can be written as $\Delta H_{\alpha\to\gamma} = \Delta H^{\circ} + \int_{0}^{T_{tr}} \Delta C_p dt$, where ΔH° is the heat of transition at absolute zero, and the integral represents the difference in the amounts of heat required to raise the temperature of the phases from zero to the transition point. If it is true that the free energy of the solid solutions can be represented by eq 1, then according to assumption 2, the magnitude of ΔH° should be, using the author's values:

$$\Delta H^{\circ} = \tfrac{1}{2} N V_{m.u.} (Z_{\gamma}\text{-}Z_{\alpha}) = \frac{94{,}000}{12} (12\text{-}8) = 31{,}000 \text{ cal per mol} \quad [5]$$

Using enthalpy data for pure iron,[*] $\int_{0}^{T_{tr}} \Delta C_p dt = -742$ cal per mol, it appears therefore that:

$$\Delta H_{\alpha\to\gamma} = 31{,}000 - 742 = 30{,}000 \text{ cal per mol} \quad [6]$$

Since the experimental value of $\Delta H_{\alpha\to\gamma}$ is about 200 cal per mol, it is evident that if eq 1 holds, then the assumption of equality of bond energies in the α and γ phases is not justified.

When the true criteria for phase equilibrium are applied, the fallacy of the assumptions becomes apparent. Eq 2 is not a complete statement of the common tangent rule, since equality of the first derivatives is a necessary but not a sufficient condition for the existence of a common tangent. It is also necessary that:

$$\left[F - C\left(\frac{dF}{dC}\right)\right]_{\alpha} \quad \left[F - C\left(\frac{dF}{dC}\right)\right]_{\gamma} \quad [7]$$

Both conditions, in general, cannot be satisfied with free energy curves based upon the author's assumptions. This is illustrated in Fig. 7 by the free energy curves for the α and γ phases in the Fe-Ni system, calculated from eq 1 in accordance with the assumptions in this paper, using values of the appropriate constants from p. 1205 of ref. 10.* Obviously, it is impossible to draw a tangent common to both curves.

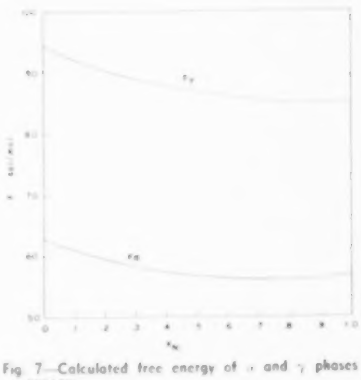


Fig. 7—Calculated free energy of α and γ phases at 1000°K.

In view of these considerations it is difficult to regard eq 4 of the authors as much more than an empirical relation of approximately the correct form. Its form resembles that of the classical thermodynamic equations for ideal solutions[7] and I wonder if the author has made any attempt to apply these equations, perhaps with modifications, to predict phase boundaries? An approach to the problem along these lines might have some advantages in clarity and rigour.

E. S. Machlin (*Columbia University, New York*)—In the statistical treatment of binary alloys there are two conditions which must be used to define the compositions of the two phases that are in equilibrium. These two conditions are that the slopes of the tangents to the free energy vs. composition curves for the two phases, at the equilibrium compositions, must be equal (eq 2 of the text) and that these tangents must have the same intercept at the pure state. Analytically, the latter condition may be expressed as:

$$F_{\alpha} - C_{\alpha}\frac{\partial F}{\partial C} = F_{\beta} - C_{\beta}\frac{\partial F}{\partial C} \quad [8]$$

[*] The term K_1T_1 in eq 1 is not included in the free energy curves. Data on p. 426 of ref. 10 show that $K_1T_1 - K_2T_2 \approx 1500$ cal per mol. These terms cannot significantly alter the relative positions of the curves.

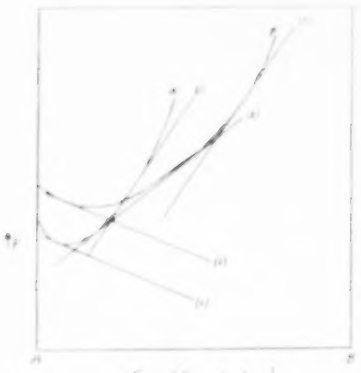


Fig. 8—Demonstrating that $\frac{\partial F}{\partial C}_{\alpha} = \frac{\partial F}{\partial C}_{\beta}$ is a necessary condition for equilibrium between the α and β phases but not a sufficient condition. Lines 1, 2, and 3 all obey this condition, but all do not define the compositions that are in equilibrium.

The first condition is necessary but not a sufficient condition as illustrated by Fig. 8. Thus, the solutions of eq 4 of the text are not necessarily the equilibrium compositions C_α and C_β.

It is worthwhile to set down the solutions of eq 1 of the text obtained by applying the two conditions (eq 2 and eq 3). In obtaining these solutions the only assumption made is the usual one, namely that $K(T)$ is independent of composition. The resulting equations are:

$$RT \ln \left[\frac{1-C_\beta}{1-C_\alpha} \right] = \Delta F^\circ + N_v[Z_v V_v C_\alpha^2 - Z_\beta V_\beta C_\beta^2] \quad [9]$$

and

$$RT \ln \left(\frac{C_\beta}{C_\alpha} \right) = \Delta F^\circ + \Delta F_s + N Z_\beta V_\beta (C_\beta^2 - 2C_\beta) - N Z_\alpha V_\alpha (C_\alpha^2 - 2C_\alpha) \quad [10]$$

where

$$\Delta F_s = \frac{N_v}{2}[Z_\beta(V_{\beta\beta}) - (V_{\alpha\alpha}) + 2V_\alpha) - Z_\alpha(V_{\alpha\alpha}) - (V_{\alpha\alpha}) + 2V_\alpha)]$$

$\Delta F^\circ = (F^\circ_\beta - F^\circ_\alpha)$ is the free energy released on transferring one mol of the pure matrix from the α to the β phase.

Using eqs 9 and 10 the assumption of Zener[2] and the author in terms of the nearest-neighbor approximation of binary alloys can be understood. Zener[2] assumed ideal solution in both the α and γ phases. This assumption analytically may be represented as:

$V_{\alpha\alpha} = V_{\beta\beta} = 0$, i.e., the heat of mixing is zero.

In this case Zener's equations can be obtained from eqs 9 and 10, where it is assumed that $\ln (1-C) = -C$, namely that

$$C_\beta - C_\alpha = \frac{\Delta F^\circ}{RT} \quad [11]$$

and

$$\frac{C_\beta}{C_\alpha} = \exp \left[\frac{\Delta F^\circ + \Delta F_s}{RT} \right] = \exp \left[\frac{\Delta F_s}{RT} \right] \quad [12]$$

It is interesting to note that eq 12 implies that the ΔF°, which Zener assumed to be independent of temperature, is really dependent upon temperature, inasmuch as ΔF° is temperature dependent. For the most part Zener's quantitative conclusions are not materially affected because in the temperature range of interest ΔF° is an order of magnitude smaller than ΔF_s.

Professor Rostoker's assumptions are that

$$(V_{\alpha\alpha})_{C_\alpha} = (V_{\alpha\alpha})_{C_\beta} (V_{\beta\beta})_{C_\alpha} = (V_{\beta\beta})_{C_\beta} V_{\alpha\beta} = V_\alpha$$

Applying these assumptions to eqs 9 and 10, the following is obtained:

$$RT \ln \left[\frac{1-C_\beta}{1-C_\alpha} \right] = -\Delta F^\circ + N_v V_\alpha [Z_\alpha C_\alpha^2 - Z_\beta C_\beta^2] \quad [13]$$

and

$$RT \ln \left[\frac{C_\beta}{C_\alpha} \right] = \Delta F^\circ + \Delta F_s + N_v Z_\beta V_\beta (C_\beta^2 - 2C_\beta) - N_v Z_\alpha V_\alpha (C_\alpha^2 - 2C_\alpha) \quad [14]$$

There is but one adjustable parameter in Zener's eqs 11 and 12 and there are two adjustable parameters in Rostoker's eqs 13 and 14. In view of this and the simplicity of Zener's assumptions relative to those of Rostoker, it is this writer's opinion that the last paragraph of Dr. Rostoker's paper is unjustified.

William Wilson, Jr. *(Elco Products Co., Chicago)*—Dr. Rostoker has applied the free energy equations derived with the usual simplifying assumptions to represent certain phase boundaries in binary systems. Most of the theoretical phase relationships taught in classrooms are based on these free energy equations which, herein, have been applied to actual phase diagrams.

The assumption of constant bond energies between two A atoms, two B atoms, and an A and a B atom is rapidly gaining momentum in metallurgy. The assumption of these constant bond energies independent of the other surrounding atoms, phase structure, temperature, and composition warrants additional consideration.

The author's eq 2 includes only the first equality of those derived from the minimum free energy principle. The complete set of equalities is:

$$\left(\frac{\partial F}{\partial c} \right)_\alpha = \left(\frac{\partial F}{\partial c} \right)_\beta = \frac{F_\alpha - F_\beta}{c_\alpha - c_\beta}$$

By including the second equality, it is possible to split the author's eq 3 into two component equations. Whereas the author's equation permits only the evaluation of V and $(V_{\alpha\alpha}$ and $V_{\beta\beta})$, one of the component equations permits the evaluation of $V_{\alpha\alpha}$ and V and the other of $V_{\beta\beta}$ and V. Obviously, these component equations permit all of the bond energies to be explicitly calculated.

The discusser has in preparation a paper reviewing the calculation and calculated values of these individual bond energies.

R. A. J. Shelton and **D. Summers-Smith** *(Associated Electrical Industries, Ltd., Aldermaston, Berkshire, England)*—Eq 4 of Rostoker's paper is a form of the differentiated free energy equation for a disordered solid solution, simplified by assuming that the bond energies between like and unlike atoms do not vary with temperature. This assumption does not appear to the writers to be justified. In the case of the Fe-Ni diagram, values of $K_1 = (\frac{1}{2}N(V_{11} - V_{22}))$ and $K_2 = (NV)$ obtained by selecting from Owen and Sully's diagram data for different pairs of temperatures within the temperature range 400° to 800°C vary markedly. For instance, K_1 varies from −643° to −870° (it is assumed that the negative sign for the value of K_1 has been omitted in error in the paper) and K_2 from 32° to 404°, depending on the two temperatures chosen. If the values $K_1 = -870°$, $K_2 = 404°$ are used, there is no real solution for eq 4 at 600°C. These values have been obtained from solubility data assumed at 800° and 700°; the fact that there is no solution to eq 4 at 600° shows that extrapolation cannot be used with safety. This limits the use of the equation to an interpolation formula, and in the case of the Fe-Ni diagram, interpolated values may be as much as 3 atomic pct different from the experimental ones, depending on the data assumed in the derivation of K_1 and K_2. It is doubtful whether the labor involved in the analysis adds anything to the solubility curve obtained by drawing the best curve through the experimental points.

Perhaps the author would explain why coordination No. 12 is used in the equation on p. 1205 and not coordination No. 8, which would appear to be equally valid.

Presumably the final column in Table I should refer to K_c as calculated from the molar cohesive energy equation, and not from eq 4 as stated.

W. Rostoker (author's reply)—The volume of discussion is taken as indicative of the lively interest in the subject. It appears that the true intentions in presenting the paper have been generally misunderstood for which the author would accept a large measure of blame. It was intended, and by whatever assumptions were necessary, to develop, however semi-empirical in nature, a relationship which could be used in somewhat the same manner as the Le Chatelier equation is used to represent certain other specific phase boundary types. In the light of this, the author does not feel that challenges of justification of assumptions require individual reply. Several contributors emphasize the second condition for phase equilibria which was not used in the development of the analytical representation. The author was not unmindful of this second condition but found no extra benefit from its use.

Professor Machlin's expansion of the second condition is a useful contribution. However, it should be pointed out that the single adjustable parameter equation presented at the end of his discussion was possible only through the use of a further ad hoc assumption, namely, that $V_\alpha - V_\beta = 0$ whereas the author chose only to assume that $V_\alpha = V_\beta$.

Messrs. Shelton and Summers-Smith have apparently accepted the empirical nature of the relationship but find difficulty in its application. In the particular case of the Fe-Ni system, the author derived the constants K' and K_c from phase boundary data at 800° and 700°C. This was done for the very reason that led to the difficulties discussed, namely, that the lower temperature data is most likely to be in error to some extent. The author has followed the practice of using the data from the highest temperatures at which experimental work was performed because such data represents unquestionably the closest approach to true equilibrium.

As stated in the text, the coordination number of the high temperature phase of both iron and titanium was used in the calculation of K_c for the simple reason that the resultant answers provided the closest agreement with the values of K' derived from the data. The author cannot provide an explanation. The corrections to the text are proper and are acknowledged with thanks.

[8] *Metals Handbook* (1948) p. 426. Cleveland: A.S.M.

[9] S. Glasstone: *Thermodynamics for Chemists* (1947) p. 324. New York: D. Van Nostrand Co.

Zirconium-Chromium Phase Diagram

by J. T. Waber, A. H. Roberson, and M. O. Davies

DISCUSSION, F. N. Rhines presiding

R. F. Domagala and **D. J. McPherson** (*Armour Research Foundation, Chicago*)—I should like to compliment the authors for a workmanlike job in determining the partial phase diagram of a system comprised of two metals which are certainly not easy to work with. We are completing work at Armour Research Foundation on an Atomic Energy Commission-sponsored project for the determination of eight zirconium binary diagrams. Work on the Zr-Cr system has been completed and should be published within the next year. For our work, Westinghouse Grade 3 iodide crystal bar served as the zirconium melting stock. Johnson-Matthey, electrolytic chromium, specially treated for oxygen removal, was employed.

The overall constitution of the system determined at Armour Research Foundation is in very good agreement with the present work. We found a eutectic at 18 pct Cr and 1280°C, somewhat lower than the value reported. This temperature was confirmed by thermal analysis, incipient melting studies, and regular isothermal anneals. The eutectoid was located close to 1 pct Cr and 835°C by metallographic analysis of annealed specimens. Maximum solubility of chromium in β zirconium was 4.5 pct at the eutectic temperature. Chromium solubility in α zirconium was less than 0.28 pct at all temperatures. We found the compound at 53 pct to melt around 1700°C, with an open maximum, but determined its crystal structure to be hexagonal close-packed ($MgZn_2$ type). The lattice parameters were in excellent agreement with those determined by Wallbaum in 1942.

The diagrams are in substantial agreement, and part of the differences are undoubtedly due to the use of different zirconium melting stock.

M. K. McQuillan (*Birmingham, England*)—I read this paper with a great deal of interest, as it covered the same field as some work of my own.* There are a number of points in the present paper on which I would like to comment. First, I should say that I, too, used zirconium prepared by magnesium reduction of the tetrachloride and electrolytically prepared chromium, and melted the alloys in a Kroll-type arc furnace. The purity of my alloys should, therefore, be comparable with the purity of those of the present authors, and any differences in our observations would not be expected to be attributable to this cause. The differences between my observations and theirs concern the presence of the eutectic, the temperature of the eutectoid, and the melting point of the compound.

I would be very much interested in any further evidence the authors may have for the occurrence of the eutectic at 1380°C. During the course of my work I noted that a number of my alloys containing 60 to 90 pct Zr melted at about 1400°C, and for a time assumed that a eutectic occurred at this temperature as described in the paper. On further investigation, however, I found that the structures of the as-melted alloys could not be made to fit in with this interpretation of the system. If a eutectic exists in this region of the system it would be expected that the as-melted alloys would show the usual type of cast structure, i.e., dendrites of the compound plus eutectic. This, however, does not occur, as may be seen from Fig. 9. The compound seen there is not dendritic in form, and the remaining material is by no means certainly eutectic. It may be argued that a compound such as $ZrCr_2$ would not form dendrites but would tend to crystallize in geometric shapes. In this case, however, I have evidence to the contrary, as on the chromium side of the compound, where a eutectic occurs at about 1545°C, the compound formed from the liquid takes on a conventional dendritic form, and the eutectic is observed in the interdendritic spaces in the usual way. There is no reason to suppose that the compound would behave differently in an alloy lying on the zirconium side of the compound composition if a eutectic existed there too.

On examination of my as-cast specimens, I found that at 60 pct Zr the alloy consisted of massive angular particles packed closely together and parallel to each other, with a small quantity of broken up, finely divided compound between them. With increasing zirconium content, the size of the massive particles decreased, and became more comparable with those of the intergranular material, until at about 80 pct Zr (close to the proposed eutectic composition) no distinction could be made between massive particles and broken up material. I interpreted these observations as follows. On cooling from the melt the alloys on the zirconium side of the compound first enter a single-phase β solid-solution region. On further cooling, massive grains of the compound separate out along crystallographic planes, the temperature at which this process begins being lower the higher the zirconium content of the alloy. As the cooling process in the argon arc furnace is very rapid, there will be no time for the remaining β solid solution to attain its equilibrium composition, and a stage will be reached at which the solution contains more chromium than it can tolerate at the temperature in question. It will then transform suddenly, forming the broken up material observed between the massive grains. At about 80 pct Zr the temperature at which the sudden breakdown occurs is such that the primary grains of compound have had virtually no time to grow before the whole structure transforms, and a structure not unlike a eutectic appears. This is closely analogous to the behavior of Cr-Ti alloys containing 30 to 40 pct Ti. In this system a β solid solution region extends across the whole diagram between 1360° and 1400° C, a compound being formed at lower temperatures. On cooling in the argon arc furnace, these alloys break down suddenly, forming lamellar structures of compound and solid solution which can readily be taken to be eutectics at first glance. There is, however, abundant evidence to the contrary in this case.

In repeating the work on the Cr-Zr alloys, I found that I could heat the specimens containing from 60 to 90 pct Zr at temperatures above 1400° C without melting them, though I was not always successful in doing so. I was forced to assume that the melting was due to some form of contamination, though I do not regard the point as having been cleared up satisfactorily. There is a further piece of evidence I might add. On heating a series of alloys of compositions in the range 60 to 90 pct Zr at 1400°C, I found that all the alloys except that containing 60 pct Zr melted completely away. If this series of alloys were in fact being heated just above the eutectic temperature, it would be expected that those farthest away from the eutectic composition would not melt completely, but would simply show rounded areas of eutectic in their microstructures after quenching, indicating those regions which had been in the liquid state. I would be most interested to hear the authors' views on this subject, and, in particular, would like to know whether dendrites of the β solid solution appeared in their as-melted alloys containing about 85 pct Zr.

On the subject of the eutectoid temperature, I am surprised that any significant arrest point could be obtained in cooling curves of these alloys at cooling rates as rapid as 5°C per min. In titanium alloys the impurities present in magnesium-reduced material spread out the transformations occurring at the titanium-rich end of the system, and, instead of a eutectoid line, a three-phase region occurs, in which α and β solid solutions and compound coexist. By analogy, the arrest point observed by the authors, even if their cooling rate were sufficiently slow, would correspond presumably to the beginning of the three-phase region rather than to the eutectoid line. I have, however, some experimental evidence to offer on this point. An alloy lying just on the chromium side of the eutectoid composition was examined in the temperature region 700° to 900°C by the hydrogen pressure method,[5] in which transformations in alloys are followed by observing the changes in the equilibrium pressure of hydrogen in a closed system containing the alloy and a very small quantity of hydrogen. Observations are made at a series of temperatures, a number of pressure readings being taken at each temperature until no further change in pressure is observed. Thus the alloy has a good chance of being in equilibrium when the final pressure reading is taken at any particular temperature. By this method it was found that the eutectoid transformation occurred over a range of temperature from 920° to 835°C. It is expected that the transformation temperature in a pure alloy would be closer to the latter temperature than to the former. There was, however, no evidence for a eutectoid at 895°C. At this temperature the pressure readings, plotted as log p against $1/T$, lay on the straight line corresponding to the α solid solution. I feel that evidence other than that of thermal analysis is necessary before 895°C is accepted as the eutectoid temperature.

My third point concerns the melting point of the compound. I have already stated that on the chromium-rich side of the compound a eutectic reaction occurs between the compound and the chromium-based solid solution at a temperature between 1540° and 1550°C. It is difficult to reconcile this fact with the authors' observation that the compound melts at 1525°C. I have heated it to 1620°C without observing melting.

E. T. Hayes, A. H. Roberson, and **M. H. Davies** (authors' reply)—The authors wish to thank the discussers for their comments on this paper. No doubt some refinements will be made to the diagram as more work is done on the system. In general there is good agreement between the Armour Research Foundation group and the Bureau of Mines staff. Any minor variations in results can be attributed to variations in the purity of starting materials.

The variation in crystal structure is rather difficult to explain. No evidence of a hexagonal close-packed structure that could not be attributed to α zirconium was found in any of our work. Considerable difficulty was experienced in obtaining a sample of the pure compound, and it is suggested that the extra lines observed by other workers may have been the result of an impure compound.

Table III lists the important lines of the crystal structure as calculated and observed at this laboratory. It will be noted that the observed intensity values correlate very well with the calculated values, which indicates that the structure is correct, that is, face-centered cubic.

Because of the similarity of titanium and zirconium, it seems likely that the intermediate phase in both

Table III. Diffraction Data for $ZrCr_2$

hkl	A	2θ	F^2pL^2	Observed Intensity
111	4.12	21.4	1,875	2
200	3.56		0	0
220	2.54	35.2	72,000	38
311	2.17	41.5	175,000	61
222	2.07	43.6	40,000	16
400	1.80		50	0
331	1.654	55.5	1,340	Slight indication
420	1.620		0	0
422	1.470	63.2	46,900	12
333-511	1.386	67.5	87,000	14
440	1.274	74.2	72,200	9
531	1.218	78.4	8,700	2
442-600	1.20		0	0
620	1.140	85.0	24,200	4/10 change of scale factor
533	1.099	89.0	35,300	12
622	1.087	90.2	25,600	10
444	1.040	95.6	1,240	Slight indication
551-711	1.009		486	0
640	1.000		0	0
642	0.963	100.2	63,000	15
553-731	0.950	110.2	21,800	23

Copper radiation filtered through nickel filter.
Note: Observed intensity values are the number of chart divisions over background intensity. Values for lines below 620 were obtained using a larger size receiving slit. Second value on 620 line included for comparison.

systems should be similar. A comparison of the structure data of TiCr$_2$ as determined by Duwez and Taylor[3] reveals a startling similarity with the values reported in Table III, and is another basis for confirming the authors' belief that the structure of ZrCr$_2$ also is face-centered cubic.

No evidence has been developed for believing that a field of extended solubility exists, as suggested by Mrs. McQuillan. She states[4] that she was rather surprised at the region of complete solubility in the Ti-Cr system even though they were close to the 15 pct limit suggested by Hume-Rothery. Since the atomic dimensions of zirconium and chromium differ considerably more than 15 pct, it is not unreasonable to expect the result to be the normal eutectic type of diagram.

The micrograph referred to, Fig. 9, was taken at X500. At this magnification the dendritic structure of the cast material is not as apparent as it is at a lower magnification.

Melting point determinations, observed through an optical pyrometer, showed that alloys near the eutectic composition did melt suddenly in many cases.

Subsequent to the publication of the paper, additional measurements have indicated that the melting point of the intermediate compound ZrCr$_2$ should have been reported as 1650° ±10°C.

Impurities in zirconium metal, especially oxygen and nitrogen, are known to raise the transformation temperature of α to β and to spread the temperatures over a range. The zirconium used in this investigation was specially selected for low impurity content and gave lower transformation temperature values than are ordinarily obtained when standard production run zirconium is used.

We feel rather confident that the diagram as presented is essentially correct with the exception of the revised melting point of the intermediate phase.

[3] M. K. McQuillan: A Survey of the Constitutional Diagram of the Chromium-Zirconium System. Report SM-165 (January 1951) Aeronautical Research Laboratories, Department of Supply, Fisherman's Bend, Melbourne.
[4] M. K. McQuillan: Journal Inst. Metals (1951) 79, p. 379.
[5] A. D. McQuillan: Journal Inst. Metals (1951) 79, p. 73.
[6] F. Duwez and J. L. Taylor: Trans. A.S.M. (1952) 44, p. 495-517.

Constitution of Titanium-Aluminum Alloys

by H. R. Ogden, D. J. Maykuth, W. L. Finlay, and R. I. Jaffee

DISCUSSION, F. N. Rhines presiding

E. Bumps and **H. D. Kessler** *(Studebaker Corp., South Bend, Ind., and Armour Research Foundation, Chicago, respectively)*—In the region of the Ti-Al phase diagram that the authors established on the basis of metallographic data, we find them in reasonably good agreement with similar data obtained at the Armour Research Foundation. It is unfortunate that they were not able to extend their studies to higher temperatures, for if they had, they would not have shown the high temperature relationships predicted in Fig. 1.

The results of our work on the Ti-Al system are based primarily on micrographic analysis of iodide titanium-base alloys with up to 64 pct Al, annealed at temperatures as high as 1400°C. The slight difference in slope of the $\alpha + \beta$ field for the two investigations is illustrated in Fig. 19 and may be due to differences in actual composition or variations in technique. In any case, we have been able to show $\alpha + \beta$ structures extending to much higher temperatures and higher aluminum contents, Fig. 20. Also, by quenching a 25 pct alloy from the β field we obtained serrated α, indicating a transformation had taken place. On this basis, we question the authors' conclusions regarding the solubility of aluminum in β titanium for the interpretation of their Figs. 8 and 9.

Our data indicated the $\alpha + \beta$ field extended to a peritectoid reaction: $\beta + \gamma \rightleftarrows \alpha$, whereas γ was formed by the peritectic reaction: β + melt $\rightleftarrows \gamma$.

We obtained similar microstructures in the $\alpha + \gamma$ field as reported in this paper, and concur with the authors' interpretation of precipitation. Although there is good agreement with the data at 1100°C for the extent of the γ field, we found that this phase field becomes wider, rather than narrower, at elevated temperatures.

On the basis of extensive investigation of many alloys in the region between 45 and 63 pct Al, we were unable to obtain the structure shown in Fig. 15 for alloys in the 50 pct Al region. Fig. 21 illustrates the structure obtained by annealing an as-cast 49 pct Al alloy at 1100°C, the same treatment used by the authors. The structure has been interpreted as being TiAl$_2$ platelets precipitated from the supersaturated γ solid solution.

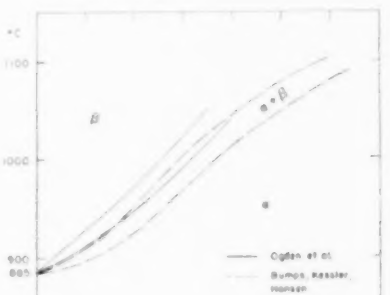


Fig. 19—Comparison of $\alpha + \beta$ phase fields.

Conversely, the structure in Fig. 15 resembles that of our 61 pct Al alloy in the as-cast condition, in which case the primary needles were γ phase and the matrix, TiAl. Upon annealing at 1100°C, the structure consisted of primary γ needles in addition to Widmannstätten platelets of γ which were rejected from the supersaturated TiAl matrix as shown in Fig. 22.

Wolfgang Gruhl *(Institute fur Metallkunde, Clausthal-Zellerfeld, Germany)*—The interesting results of this treatise are generally in agreement with the research carried out in the Institute of Metallurgy at the Bergakademie Clausthal. Several aluminothermically produced Ti-Al alloys, with titanium contents between 50 and 80 pct produced as pre-alloys to use to add titanium to make nonferrous alloys, have been investigated by microscope and X-ray diffraction. The same kinds of crystals have been found as were described by the authors. The investigated alloys contained, apart from titanium and aluminum, as impurities: 0.38 to 0.43 pct Fe and 0.56 to 0.63 pct Si.

Fig. 20—25 pct Al alloy water quenched after 6 hr at 1200 C. Structure shows $\alpha + \gamma$ transformed γ. X150. Area reduced approximately 50 pct for reproduction.

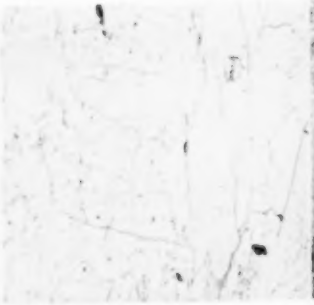


Fig. 21—49 pct Al alloy water quenched after 6 hr at 1100 C. Structure shows a fine precipitation of $TiAl_3$ in a γ matrix. X100. Area reduced approximately 50 pct for reproduction.

Fig. 22—61 pct Al alloy water quenched after 7 hr at 1100 C. Structure shows primary γ platelets with fine Widmannstatten precipitation of γ from the saturated $TiAl_3$ matrix. X100. Area reduced approximately 50 pct for reproduction.

One alloy containing 78.4 pct Ti showed pure α grains in its microstructure. Alloys containing 75.5, 72.4, 70.1, 67.3, and 66.0 pct Ti also consisted of α grains which, however, with decreasing titanium content produced increasing bands by precipitation of the γ marked phase. One alloy containing 63.5 pct Ti showed two kinds of crystals, namely the pure γ phase and α grains with banded γ precipitations. Alloys containing 57.2 and 53.3 pct Ti consisted of γ grains and Al_2Ti.

From these microstructures it may be seen that as a result of the aluminothermically produced alloys the field of the γ phase, which may be considered as the intermediate compound, $AlTi$ is far more limited than was observed by the authors. After the experiments at low temperatures, the γ field was found to extend only to 59 to 61 pct Ti while the heterogeneous fields $\gamma + \alpha$ and $\gamma + Al_2Ti$ were enlarged accordingly. The α field too is somewhat narrowed and reaches at low temperatures only about 77 pct Ti. At higher temperatures, however, the α field extends and reaches at the peritectic temperature up to 65 pct Ti. This has been proved by the fact that primary γ grains have only been observed below this concentration, while between 65 and 77 pct Ti, the γ phase is always found as a precipitate in α grains. The deviations of these investigations may be traced back to the aluminothermically produced material which contained iron and silicon.

By X ray investigation it was also found that the γ phase has a tetragonal face-centered lattice. The superlattice lines were also observed. The axial ratio of the tetragonal lattice was fixed as $c/a = 1.02$, the lattice constant was $a = 3.999$A and $c = 4.080$A. A change of the lattice constant between γ in balance with α and γ in balance with Al_2Ti could not be observed. The reason may doubtless be found in the narrow limits of the γ field.

The axial ratio of the hexagonal α lattice in balance with γ was fixed as $c/a = 1.62$, the lattice constant was $a = 2.867$A and $c = 4.645$A.

It was further observed that the precipitation of the γ phase at cooling exclusively takes place on the (0001) planes of the hexagonal α grains. This could clearly be seen in the microscope when grinding bigger grains, the orientation of which had correctly been found by Laue-X-ray-photographs, in certain crystallographic directions. Fig. 23 shows two grains of an alloy containing 66 pct Ti on which the γ precipitates owing to the various position of the (0001) planes to the surface of slide appear to be broad and fine striped alternatively. Owing to this precipitation, alloys between 65 and 77 pct Ti showed a distinct cleavability in the hexagonal, basal plane which is not more perceptible in higher titanium contents.

Fig. 24 shows the typical intergrowing of α grains at their solidification in an alloy with 66 pct Ti. The grains seem to be dovetailed into each other at their boundary. It is clearly seen that the growth direction of the hexagonal crystals passes parallel to the basic plane and are clearly recognizable by subsequent precipitation of γ on the (0001) planes.

Niels Engel *(University of Alabama, University, Ala.)*—Because the electron-gas energy-band theory has not been of much help in accounting for metallic properties, especially diagram formation, I have tried to develop a different theory which may be of some help in this respect to metallurgists. This theory has not yet been published in English and I suppose metallurgists will be interested in knowing about it. I have called it the "electron oscillator theory" to distinguish it from the electron-gas theory.

This theory postulates that the number of outer bonding electrons control the lattices of metals crystallizing with body-centered cubic, hexagonal close-packed, and face-centered cubic lattices in the same

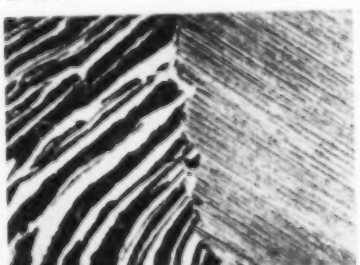


Fig. 23—γ precipitation on planes of two differently oriented grains. X150.

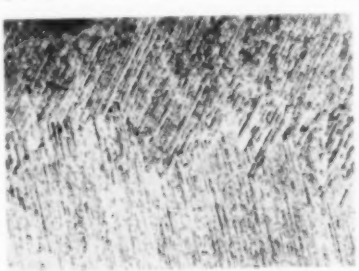


Fig. 24—Intergrowing of α grains. X150.

manner as the number of outer bonding electrons control the lattices of the (8-N) rule phases according to Hume-Rothery. One electron per atom controls the body-centered cubic lattice, two bonding electrons per atom the hexagonal close-packed lattice, and three bonding electrons the face-centered cubic lattice. This is evident from the metals, sodium, magnesium, and aluminum, respectively.

Allotropic transformations are caused by a change in the number of outer bonding electrons. In the transition metals electrons can be transferred from the outer bonding level to an inner partly filled *d*-shell, or vice versa. In the transition elements from the columns 3, 4 and 5 headed with the elements Sc, Ti and V, electrons are sucked into the *d*-shell from the outer shell when the temperature is raised. Allotropic transformations, if any, therefore exhibit lattice changes from hexagonal structures (two electrons) at low temperatures to body-centered cubic structures at high temperatures (one electron). Ti, Zr, and Hf change from hexagonal low temperature structure to body-centered cubic high temperature structure. In the transition elements from columns 6 to 8 headed with the elements Mn, Fe, Co, and Ni the opposite trend exists. Here electrons leave the *d*-shell and enter the outer shell when temperature increases. Iron changes from body-centered cubic (one electron) to face-centered cubic structure (three electrons) and cobalt changes from a hexagonal close-packed low temperature structure to a face-centered cubic high temperature structure. Reasons for these trends are given in a previous paper.[7]

Adding alloying elements to metals with allotropic transformations will influence the temperature at which the allotropic transformation taken place according to the number of outer bonding electrons. The addition of elements carrying three or more bonding electrons per atom to titanium will stabilize the hexagonal phase and push the transition to higher temperatures. Elements carrying only one bonding electron per atom will stabilize the high temperature phase and move the transition to lower temperatures with increasing amount of alloying elements. For cobalt the same principle is valid. Elements with three or more bonding electrons added to cobalt stabilize the high temperature structure and decrease the transition temperature while elements carrying one or two bonding electrons per atom stabilize the low temperature structure and increase the transition temperature.

This theory was given in a talk at Battelle Memorial Institute in 1948, and the predictions made at that time have since been proved in several cases by experiment.[7, 8] Hafnium, which was not known to possess an allotropic transformation in 1948, also obeys this rule.

The influence of elements forming interstitial solid solutions was not discussed fully in 1948 and their influence therefore was not predicted by the theory. Since this time experiments have proved to be in agreement with expectations. Interstitial atoms do not introduce new lattice points because they hide between the greater transition atoms. The bonding electrons of the interstitial atoms are given off to, or form bonds with, the bonding electrons of the lattice forming transition atoms. In elements from cols. 3, 4, and 5 these added electrons are sucked into the *d*-shell or form bonds with *d*-electrons. The added electrons will not go into the outer shell to stabilize the electron-rich phase. In neutralizing some of the *d*-electrons by pairing, the opposite effect must be expected. Interstitial atoms added to cols. 6 to 8 elements give off their electrons or form bonds with the outer electrons thus increasing the stability of the electron-rich phases.

H. R. Ogden, D. J. Maykuth, W. L. Finlay, and **R. I. Jaffee** (authors' reply)—The authors are pleased to see the results of other investigations on this interesting system. The work done by Bumps and Kessler in determining the diagram between 1100°C and the melting range is a definite contribution which fills in the temperature range not covered in this investigation. Over the ranges investigated, the two investigations are in good agreement. With regard to the discrepancy concerning the microstructure of an alloy containing 50 pct Al, it is possible that the alloy we studied was segregated and the area shown in Fig. 15 is higher in aluminum than the balance of the ingot. Since we were primarily interested in the titanium-rich region of the diagram, we did not make as extensive an investigation of the $\gamma + TiAl_3$ field as Bumps and Kessler did.

The results reported by Gruhl confirm the existence of the phases present as established by this investigation, and in the investigation of Bumps and Kessler, and also Duwez and Taylor.[9] It is probable that the impurities present in his alloys had an influential affect on the solubility limits of both the α and γ phases since the other investigations were in good agreement. The lattice constants of the γ phase determined independently by Gruhl are also in good agreement with those reported here and by Duwez and Taylor.[10] The intergrowing of α grains shown in Fig. 24 is probably caused by the β to α transformation rather than solidification since Bumps and Kessler have found a peritectoid reaction rather than the peritectic reported here.

The authors wish to thank Dr. Engel for his discussion of his alloy theory. In 1948, Engel predicted independently, through the use of his theory, that aluminum additions to titanium would raise the transformation temperature, which has subsequently been proved by this and other investigations.

[7] N. Engel: Kemisk Maanedsblad (1949) 30, p. 52.
[8] N. Engel: Kemisk Maanedsblad (1949) 30, p. 97.
[9] A. R. Elsea and C. C. McBride: Trans. AIME (1950) 188, p. 154; Journal of Metals (January 1950).
[10] E. E. Fletcher and A. R. Elsea: Trans. AIME (1951) 191, p. 897; Journal of Metals (October 1951).
[11] P. Duwez and J. L. Taylor: Crystal Structure of TiAl. Journal of Metals (January 1952); Trans. AIME, p. 70.

Solubility of Gaseous Nitrogen in Gamma Iron and the Effect Of Alloying Constituents—Aluminum Nitride Precipitation

By L. S. Darken, R. P. Smith, and E. W. Filer

DISCUSSION, F. N. Rhines presiding

E. Spire (*Consulting Engineer, Montreal, Que., Canada*)—I want to congratulate the authors for their remarkable study of this difficult problem. Do they have an idea of what happens to aluminum nitride when the steel is molten? Is it simply dissolved in the metal or dissociated, completely or partially?

H. F. Beeghly (*Jones and Laughlin Steel Corp., Pittsburgh*)—The various metal-nitrogen systems in commercial steels and their behavior during thermal treatment have been subjects of growing importance to producers and fabricators. In recent years, these systems have been explored with renewed vigor and fresh approaches. The authors' paper represents one of the results of this renewed interest.

Table IV shows the effect of silicon contents up to 0.58 pct on lowering the solubility of nitrogen in

austenite; the authors point out that, with higher silicon, difficulty was experienced in equilibrating the steels with the nitrogen atmosphere, but that, in general, with increasing silicon contents up to 3.48 pct a smaller amount of nitrogen was absorbed. They ascribe this difficulty to an oxide film. The existence of an "acid insoluble" nitrogen compound in the steels with the larger silicon contents would result in an apparent lowering of the nitrogen solubility unless the analytical method was modified to give a total nitrogen value. I am wondering if the authors would care to comment on this as a possible explanation for the seemingly erratic behavior of the higher silicon steels, and also whether their experience indicates that the oxygen content of the metal influences the solubility and rate of solution of nitrogen. It likewise would be of interest to know the aluminum content of these steels, since this element has a very pronounced effect on the behavior of nitrogen in steel.

The earliest reference to the structure of aluminum nitride (AlN) that has come to our attention is that of Ott[9] in 1924. His powder data on prepared samples and ours on aluminum nitride extracted from steel[10, 11] agree very well and are given added support by the present authors, who are to be congratulated for their careful experimental work and its orderly presentation.

L. S. Darken, R. P. Smith, and **E. W. Filer** (authors' reply).—In reply to Mr. Spire's question, there is little doubt that aluminum nitride has a high solubility in molten iron or steel; that is, if added in moderate amount to molten iron or steel it would yield a homogeneous solution. There is no reason to believe that this solution would contain molecules of aluminum nitride, especially since the nitride phase itself is not molecular. An excellent description and diagram of the atomic arrangement in an Fe-Cu-S melt has been given by Rosenqvist and Cox,[12] presumably an Fe-Al-N melt would be of analogous arrangement. Experimental work on the solubility of nitrogen and of aluminum nitride in molten Fe-Al alloys would be of interest in this connection; this is beyond the scope of the present report.

We do not fully understand Mr. Beeghly's suggestion of an "acid insoluble" nitrogen compound. It is true that Si_3N_4 is not always dissolved by hydrochloric acid, particularly if the silicon content of the iron or steel is high. In view of this Mr. Momeyer, in analyzing our samples containing silicon, used a mixture of hydrofluoric and hydrochloric acids for solution; there was never any indication of an undissolved nitride residue. In treating the alloys of Table IV with an ammonia-hydrogen atmosphere at about 600°C, we found (in work to be reported subsequently) that about 1 pct N could be introduced into the alloy, precipitating the silicon almost quantitatively as Si_3N_4. There was no trouble in dissolving this nitride completely in the acid mixture; this was verified to our satisfaction by the fact that, for equilibrated specimens, the nitrogen content of each specimen bore the same ratio to the silicon content as would be anticipated on a stoichiometric basis, allowing for the relatively small solubility of nitrogen in silicon-free ferrite.

We have found, in accord with the experience of others, that a layer of surface oxide acts as a highly impermeable barrier to nitrogen penetration. We have found no evidence that minor oxide inclusions in the metal have appreciable effect on the solubility or diffusivity of nitrogen.

It is indicated by analysis that the aluminum contents of each of the alloys of Table IV are 0.006 pct or less. As may be seen from Fig. 4, this is not sufficient to influence the equilibrium nitrogen content at the temperatures under consideration.

[9] H. Ott: The Lattice of Aluminum Nitride. *Ztschr. Physik* (1924) 22, pp. 201-214.

[10] H. K. Work and G. H. Enzian: Effect of Deoxidation on Strain-Sensitivity of Low-Carbon Steels. *Trans.* AIME (1945) 162, pp. 729-731.

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Constitution and Properties of Some Iron-Bearing Cupro-Nickels

by F. W. Pellow and F. G. Wilson

DISCUSSION, F. N. Rhines presiding

G. L. Bailey (*British Non-Ferrous Metals Research Association, London, England*).—I was glad to see this further work on the structure and properties of the Cu-Ni-Fe alloys of low nickel content in which we have been so interested in the United Kingdom since before the war.[1]

The authors' data on the variation in solubility of iron in both 5 and 10 pct Ni alloys with temperature is based on more detailed observations than we have made but is generally in line with our own work. The difficulty in these matters is in the identification of the structures obtained. The precipitation of the second phase which we presume to be the α' solid solution, richer in nickel and iron, from the α solution with which it is in equilibrium occurs in such a fine state of division that its resolution by ordinary micrographic methods is impossible in the early stages. We have published[2] some electron micrographs which illustrate the effects observed more clearly but we agree with the authors when they say that dark staining characteristics when the alloys are subjected to seawater corrosion are more sensitive in detecting the presence of the α' phase than is the microscope.

After taking this point into consideration, however, I confess to some difficulty in understanding Fig. 4. I can only assume that the precipitates visible at such a low magnification as 150 diam in these relatively coarse forms are produced from iron-rich areas of the initial solid solution due to inadequate homogenization. If this is so I find it difficult to accept the authors' contention that such local variations in iron concentration as are capable of giving the heavy precipitates shown in Fig. 4 do not in fact materially affect the solvus surfaces of their equilibrium diagrams.

I share the authors' enthusiasm about the resistance to corrosion of these alloys by seawater but I am not fully in agreement with them on the vexing question of the best iron content for these alloys. In Fig. 3 of ref. 8, we give many results showing that the resistance of these alloys to impingement attack in the Jet Test increases as the iron content rises to 2 pct. With higher iron contents pitting at shielded areas is likely to occur. Admittedly the addition of 0.75 pct Fe produces a large improvement in corrosion resistance compared with a pure 90/10 Cu-Ni alloy, but the further improvement on raising the iron to 2 pct is substantial. We recommend from 1.5 to 2 pct Fe as the desirable range from the point of view of corrosion resistance.

While it is true that British practice generally uses a hard tube, the corrosion resistance of the 10 pct Ni alloys has in our work been little affected by the structural condition. Although the annealed alloys blacken in seawater, this effect seems to be superficial and not to be accompanied by any real decrease in

corrosion resistance as is the case with the 5 pct Ni alloys. I admit however that there may prove to be some justification for the authors' suggestion that this point is affected by the degree of pollution of the water. We also lack firm evidence.

There is, finally, a point I should like to raise on which the authors do not touch. In certain circumstances, it seems that grain boundary separation of α can result in an intercrystalline weakness in the alloys which is revealed by severe working of material in a susceptible condition. This hardly affects the manufacture or use of condenser tubes but may show in certain severe coppersmithing operations. Have the authors encountered anything of this nature?

E. W. Palmer and **F. H. Wilson** (authors' reply)—It is unfortunate that our manuscript was completed before the comprehensive and valuable work reported by Mr. Bailey became available in this country. Mr. Bailey's discussion is a welcome one, since it points out both areas of agreement and of possible disagreement in the two investigations.

With regard to precipitation of the iron-rich phase, Mr. Bailey, on the basis of the fine state of subdivision of the precipitate which is shown in his own excellent electron micrographs, fears that the precipitates which we show in Fig. 4 as resolvable at 150 diam are evidence of a local iron segregation. In none of our samples was there as sharp a gradient of iron concentration as would be required to account for the precipitation shown at the boundaries of new grains in Fig. 4. Iron-rich areas due to coring would be elongated in the direction of rolling and would have appreciable breadth with a gradual concentration gradient. The magnetic colloid pattern in Fig. 7a, where the rolling direction is vertical, demonstrates these characteristics. The distribution of precipitate in Fig. 4 appears to be across the rolling direction since it occurs at the boundaries of the tiny new grains which are found in "deformation bands" which characteristically line up in a transverse direction.

Precipitate size, and hence its resolution, is more a function of the degree of supersaturation and the rate of diffusion of iron, than of the iron concentration. Perhaps our text should have emphasized our observations that this relatively large, optically resolvable precipitate (exaggerated, as it is, by electropolishing) is typically found in samples annealed above 650°C, see Fig. 6a. It is, therefore, not found in 10 pct cupro-nickels with less than about 1¼ pct Fe. Mr. Bailey has shown particles which are appreciably larger (equivalent to about 0.1 mm at 150X) in a sample of a 5 pct Ni-1.3 pct Fe alloy slowly cooled to 700°C, his Fig. 15,[7] and we believe that any samples of suitable iron content which he may have quenched and reheated to 700°C would have shown precipitates of the same order of magnitude as we show, Fig. 4. We are sure he does not consider the grain boundary precipitates in his Fig. 15 as evidence of a high local iron concentration.

The differing conclusions arrived at in the two investigations, with regard to the most suitable iron content for the 10 pct Ni alloy, result largely from differences in condenser tube practices in the United Kingdom and the United States. This point was touched on briefly in the addendum to our paper. We agree that a further improvement in corrosion resistance results from increasing the iron content from 0.75 to 2.0 pct, provided the iron is retained in solid solution. Fig. 3 of Mr. Bailey's paper refers to specimens quenched from 850°C, and iron contents up to about 3 pct should therefore be in solid solution. It is perhaps significant that in this figure Mr. Bailey has indicated a trend toward increased impingement attack of the higher iron specimens that would have contained free iron. In any case, since our paper was presented additional evidence from actual power plant service tests has strongly confirmed the harmful effect of free iron in condenser tubes supplied with polluted coastal waters. We therefore feel that the iron content should be limited to the amount that can be retained in solid solution during normal condenser tube fabrication. In British practice, where a hard drawn tube is used, the necessary quench from high temperature, and thorough pickling of the subscale formed, may be carried out on a short tube of fairly heavy gage that is subsequently drawn to finish dimensions. With this practice iron contents appreciably above 0.75 pct may be retained in solid solution in regular production. But in United States practice, where a relatively soft tube is required, the length of the tube, the thinness of gage, and the limited final reduction permitted, all conspire to make quenching from a high temperature, and thorough removal of the subscale so formed, quite impractical. We are still of the opinion expressed in the paper, that 1.0 to 1.25 pct Fe represents the maximum level at which complete solubility of the iron content can be assured in regular commercial production in this country. It should be mentioned, as emphasized by John R. Freeman, Jr., Technical Manager of American Brass Co., in the oral discussion following presentation of our paper, that these 10 pct cupro-nickel tubes are regularly supplied, in this country, with a final reduction of 10 to 15 pct, primarily to harden the tube enough to prevent accidental damage in handling.

The final point raised by Mr. Bailey has to do with "intercrystalline weakness" of these alloys that may show up during certain severe coppersmithing operations. We have not encountered this in our studies, and indeed, a series of single blow forging tests (with a 50 lb hammer falling 4 ft onto a ½ in. diam x ¾ in. tall specimen) failed to give any evidence of failure with 10 pct cupro-nickel specimens containing up to 2 pct Fe tested at temperatures ranging from 650° to 850°C. However, it has been our experience that precipitation hardening alloys are often fragile in the range of temperatures where precipitation can actually occur, and it would not be surprising if alloys of high iron content, with substantial amounts of iron in solid solution, were to develop intergranular ruptures at some critical rate of strain during coppersmithing operations. Such failures would seem less likely with lower iron contents, and this is perhaps another reason why alloys of moderate iron content may some day prove to be more practical than those in which a maximum iron content has been used to obtain a fractional increase in corrosion resistance.

[7] British Patents 557065 (1939) and 578283 (1943).
[7] Journal Inst. Metals (1928) **40**, p. 141.

Viscous Creep of Gold Wires Near the Melting Point

by F. W. Bailey, E. E. Fara, and H. Udin

DISCUSSION, M. A. Williamson presiding

A. P. Greenough (*University College, Swansea, Great Britain*)—I have recently made some experiments on the deformation of silver wire at high temperature in an atmosphere of oxygen-free nitrogen.[8] The observations which I made confirm the main conclusion of this paper, that the most satisfactory mechanism so far suggested to explain the deformation which takes place

under low stresses is the diffusion of vacant lattice sites from the surface of the wire to the grain boundaries. The highest stress applied to the silver wires was 9×10^7 dynes per sq cm, and there was no evidence that crystallographic slip occurred in any of the specimens. Kinking was observed in the silver wires, but there was no evidence of any axial rotation of the grains. No bulges developed in the wires.

However, the main feature of the silver wire experiments was the lack of reproducibility of the strain measurements. There were two distinct effects. Specimens made to be as nearly alike as possible gave strains which differed, by factors up to two, on being annealed simultaneously. The rate of strain of a given specimen seemed to vary with time. It is interesting to see that both these effects appear to have been noticed in the work on gold wires. The results given in Fig. 2 show that the strains measured in the two pairs of wires carrying identical loads varied by a factor of the order of two. In the text it is suggested that the strain rate begins to decrease after a time and may eventually become zero at a limiting value of the strain.

Both effects were investigated in some detail for the silver wires. Temperature differences between various parts of the furnace would acount for variations in the behavior of similar specimens, but the effect was too large to be completely explained in this way. According to Herring's work,[3] the observed strain should vary inversely as the length of the grains in the wire, but there seemed to be no correlation between the average grain lengths of the specimens and the observed strains. The extent to which kinks and offsets develop in different specimens will influence the measured strains, but the differences were again too large to be explained in this way.

Experiments in which silver wires were heated for a long period of time were difficult to interpret, as it was found that the temperature control was rather unsatisfactory, errors up to 20° C arising over a period of weeks. However, wires in which the applied stress was negligible were heated for periods up to 750 hr, and there was no indication of an approach to a limiting strain value, although the strain rate decreased during the first 100 hr. A series of wires carrying a range of loads showed a second definite trend. As the time of annealing increased, the applied load for zero strain increased, and wires which at the start of the experiment were extending, began to contract. This is equivalent to a rise in the apparent value of the surface energy. The effect was surprisingly large. After about 200 hr at the high temperature, the surface energy had apparently increased to two or three times its original value. Several experiments gave this result.

It would be interesting if these phenomena are found in other metals, particularly copper. The statement in the present paper, that the reported increase of viscosity with the decreasing radius of copper wires is now regarded as insignificant in view of the relative lack of refinement of the earlier experiments, makes a reassessment of accuracy of the results of that experiment desirable.

Assuming that these effects are general, and are not due to imperfect experimental conditions, it is apparent that the present simple theory will have to be extended or modified. The values of the surface energies of solid copper,[7] silver,[7] and gold,[7] obtained by this method agree well with the values to be expected from measurements on the liquid metals,[8] and with the values calculated for the solids.[9,10] In the case of copper, the result is consistent with the value obtained by quite a different method.[9]

It is difficult to conceive of any other effect which would cause the specimens to contract. This particularly applies to those loaded specimens which at first extend, but after a period of about 50 hr, begin a contraction which apparently continues indefinitely. It seems unreasonable to suggest that the surface energy increases with time to the extent required to explain the results. Any contamination of the surface should lower the surface energy.

The observed strain rate is of the order of that calculated by Herring on the assumption that vacant lattice sites diffuse between the surface and the grain boundaries, and other evidence confirms the importance of this mechanism.[3] However, this does not preclude the possibility of one or more other mechanisms operating simultaneously. It is tempting to suggest that the increased strain rate in the initial stages of the experiment is related to the microcreep observed by Chalmers [11] in his single crystals of tin. The grain boundaries in the polycrystalline tin specimens which did not show microcreep were longitudinal. In the thin wire experiments, the grain boundaries are transverse.

It has long been realized that edge dislocation can act as sources or sinks for vacant lattice sites. This could be the cause of microcreep in single crystals. Nabarro[4] rejected this suggestion on the grounds that the activation energy necessary to create a vacant lattice site on the edge of a dislocation is larger than for an external surface, and too large for the rate of the process to be appreciable. Other authors, for example Seitz,[5] assume that the activation energies are approximately the same. Such a mechanism would show many of the characteristics of microcreep. The limiting strain would correspond to the exhaustion of suitable edge dislocations. As each dislocation grows or shrinks in its own plane, the strain would cause the crystal to bend slightly. Longitudinal but not transverse grain boundaries would inhibit the bending, and thus inhibit the microcreep.

It is evident that more experimental work on high temperature deformation may yield much useful information. Experiments in which the behavior of single crystals is compared with specimens having only transverse grain boundaries, and with specimens having longitudinal grain boundaries, would be particularly interesting. Some results on these lines have been obtained for silver,[7] but experimental difficulties prevented measurements being made until the specimens had been at high temperature for more than 100 hr.

F. H. Buttner (authors' reply):—It is always reassuring to find one's experiments confirmed by independent work done in other laboratories. Dr. Greenough's communication comes as welcomed news that puts greater confidence in the work now being done, as well as in future experiments presently under consideration.

It is felt, however, that in interpreting these experiments, caution should be exercised in drawing conclusions from the agreement between experiment and theory. The important finding here is that although the mechanism explains the observations, the observations do not necessarily prove the mechanism. The fair conclusion is that the wires deform by a means of what is effectively a Herring-Nabarro mechanism within the stress range and time periods used.

What appears to be a serious objection to the Nabarro-Herring mechanism is that it cannot explain: 1—diminishing strain rate with time, and 2—limiting strain, without introducing hypothetical modifications. These modifications are reasonable, but unproven, and as such leave the quantitative argument somewhat unsettled. Diminishing strain rate with time and limiting strain were observed with gold wires in some preliminary tests. Indications are that the same properties hold for silver wires in our experiments.

The side items brought up by Dr. Greenough are real ones and are certainly worth discussing. These issues include: 1—the lack of strain reproducibility in two separate wires identically loaded, and 2—the peculiar elongation followed by shrinkage observed in some wires. Both of these effects were noted by Dr. Funk and me in the early stages of our work on silver. It took considerable time in conducting many experimental variations before we felt reasonably sure that the difficulties were understood and the problem solved.

The anomalous strain behavior in silver was the first difficulty we faced. At the start, we bought fine silver wire of acceptable high purity from a reputable house. We observed in our first tests that the wires first elongated and then shrunk just as Dr. Greenough observes. That is, the stress-strain line showed an initial positive vertical displacement, and later settled to a lower position, around which crossover point the line rotated counterclockwise with time. This came as a shock, since no such observations were previously made on copper. The temptation was, of course, to attribute phantom properties to the surfaces of silver wires to explain this behavior. Dr. Wulff, although impressed by these explanations, remained unconvinced and suggested that dissolved oxygen may cause the effect. Since oxygen is highly soluble in silver, and these oxygen percentages are not reported in the ordinary chemical analyses, it could reasonably be expected that high purity silver melted in air would carry appreciable amounts of oxygen. Wire drawn from such billets and heated in the oxygen-free furnace atmosphere, may first precipitate oxygen within the wire to create an elongation, while dissipating the oxygen by diffusion. Once being oxygen-free, the wire would shrink or elongate further at a rate depending on its load. To make a long story short, we melted and cast high purity silver into a small billet in vacuum and had wire drawn from it. The first string of wire was, unknown to us, drawn by the contractor from a piece cut from the pipe of the billet, and had longitudinal holes down the length of the wire. Highly loaded specimens of this wire initially shrunk, but gradually went into an elongation while the zero strain point drifted gradually to lower stress levels with time. The wires simply shrunk while the longitudinal holes were sintering shut. Finally, this was realized and a string of wire was drawn from a sound portion of a vacuum-cast billet. With this set of wires, all apparitions disappeared, and the silver wires began to behave like the previous copper wires.

As another check, we ran some of the first wire in hydrogen. The presence of oxygen dissolved in these was shown by the occurrence of hydrogen embrittlement, which was unmistakably evident by the silver crucible's falling apart, and the wire's elongating and twisting like Chinese ashes.

I suggest, therefore, that Dr. Greenough's observed strain anomalies are due to dissolved oxygen in his high purity silver wires.

The other difficulty observed by Dr. Greenough concerns the lack of reproducibility of strain in specimens made to be as nearly alike as possible. For this, he cites several experimental causes, which are reasonable and should be eliminated from his technique. In our experiments, we had no similar thermal gradients either in time or geometry, yet like loaded wires were observed to vary in strain. The more refined strain measuring technique reduced human error to a minimum and apparently emphasized the effect in these relatively shorter gage length specimens.

Even though two wires may be taken from the same spool, loaded alike, and run together in a test with the smallest separation in position possible, the wires are not alike, because the distribution pattern of small amounts of impurities can vary along the wire. The microstructure of a given segment of wire will depend on the nature and distribution of impurities in that segment. Since the distribution of impurities may not be the same in all segments, even adjacent ones, in a spool of wire of very low impurity concentration, the microstructure of the wires will accordingly vary. Chalmers and also Herring and others have shown that the creep rate is sensitive to microstructure.

The microstructure of these wires are always described as being "bamboo," where each grain is a cylinder in contact with its neighboring grain through a flat grain boundary interface running across the wire and perpendicular to the axis. The bamboo structure is the lowest energy structure for a fine wire of high purity, and that structure predominates in these specimens. However, in localized impurity regions, grain boundaries can become hung up in the manner of Fig. 7. In both cases, the planes intersecting at line *mn* are at 120° to one another, and are stable. Chalmers has shown that over lengths of bicrystals where the interface is parallel to the axis of load, as in the case for plane *mnop* in Fig. 7a, no microcreep occurs. Therefore, whenever this configuration appears within a gage length, it effectively shortens the gage length by at least the distance *mp*. Since it is impracticable to compensate for these configurations, in any present measuring technique, the strains and strain rates so measured are in error on the low side. It is reasonable to assume that configurations of the type in Fig. 7b have a lesser effect in the same direction.

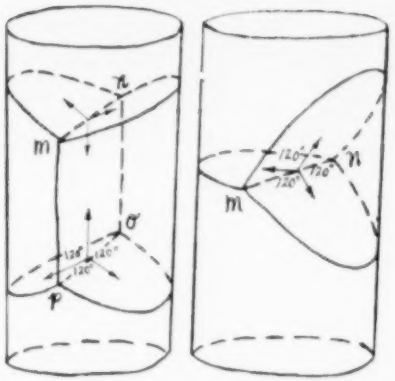

Fig. 7—Diagram showing stable grain formations.

Our summary position in this matter is that since impurity concentration variations along the length of high purity wire are random, no two gage lengths have the same periodicity of local concentration along the length. Thus, the microstructure varies with the number of Fig. 7 departures, which are different in number for two wires otherwise the same. The effective gage length is accordingly variable. Since it is impossible to compensate for this in measuring, the strains will more probably be unlike, in varying degrees, than alike.

Since this is a random perturbation, it seemed more reasonable to treat the data statistically than to base conclusions on the unpredictable behavior of individual wires. It is largely on these grounds that the data in the paper was handled as it was, by averages, least squares, etc.

Since no wire is perfect, and all carry these departures to some extent, the overall effect is to give slower strain rates, or higher viscosity than the theoretical ideal. It is felt that this is the principal reason why the experimental viscosities of Fig. 4 are slightly higher than the Herring theoretical.

This condition should have no bearing on the crossover point, since the effect is to cause the stress-strain line of Fig. 2 to rotate around the crossover point counterclockwise at a slower rate.

I would like to take the liberty of answering a previous informal criticism of the paper in this discussion. There has been some feeling that the choice of the word "microcreep" is unfortunate in this particular application, because of an ostensible difference in mechanism between gold at high temperature and single crystals of tin at low temperature. To my understanding, the term applies to the observed effects of: 1—creep strain proportional to stress, 2—decreasing strain rate with time, and 3—limiting maximum strain. The position the authors take is that any creep system that manifests the above properties is undergoing "micro-

creep." Any number of mechanisms have been, and may yet be, proposed which will explain the above properties. These, at the moment, include slow moving dislocations, subcell boundary movement, and modified interpretations of Nabarro's mechanism. One Nabarro modification does fit Chalmers' microcreep data. Quantitative arguments for each are seen to hinge on only one measurable quantity, the activation energies, which turns out to be about the same regardless of the mechanism. Therefore, since no mechanism has been fully proven, it seems wiser to define the word "microcreep" on its original property basis rather than any mechanistic one.

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[10] R. Fricke: Ztschr. Physikal Chem., (1942) (B) 52, p. 284; also Ztschr. Elektrochem., (1946) 52, p. 72.
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Vapor Pressures of Zinc Over AgZn Alloys

by J. F. Elliott and R. A. Swalin

DISCUSSION, W. A. Williamson presiding

P. Herasymenko (*New York University, New York*)—The partial molar thermodynamic properties of zinc (referred to liquid zinc) calculated from the data of the authors are given in Table III. A very sharp decrease in H_{Zn} and S_{Zn} after about 50 pct Zn seems to indicate that the degree of order in the homogeneous β phase changes very considerably within the range of a few atomic percent zinc. It would be interesting to know if there are corresponding changes in the physical properties of the alloys (e.g., in the electric conductivity) and in the X-ray data.

Table III. Partial Molar Thermodynamic Properties of Zinc

Atomic Pct Zn	$\bar{F}$ in agreement at 670°K, Cal per Atom	$\bar{H}_{Zn}$, Cal per Atom	$\bar{S}_{Zn}$, Cal per Atom per Deg
43.4	2840	1890	1.98
50.4	2010	1280	1.33
54.7	1550	1700	0.17

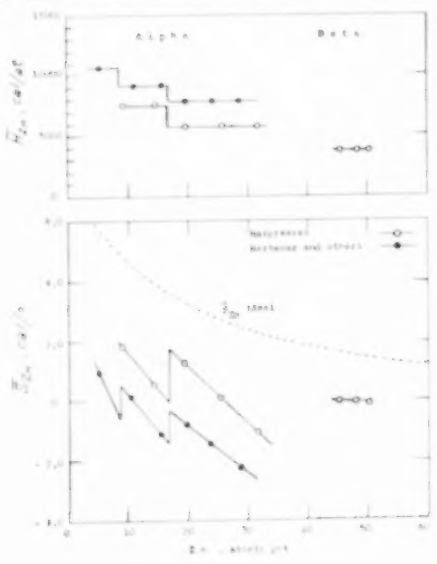


Fig. 8 (left)—Partial molar heat, $\bar{H}_{Zn}$, and partial molar entropy, $\bar{S}_{Zn}$, in CuZn alloys.

It is usually assumed that partial thermodynamic functions vary continuously with the composition of a homogeneous phase. The writer is of the opinion that discontinuous changes in these functions at certain composition of a solid solution occur frequently, but were overlooked in previous investigations. An examination of the data on the vapor pressures of zinc over CuZn alloys reported by Hargreaves (dew-point method) and by Herbenar, Siebert, and Duffendack (absorption-spectra method) can be taken as a confirmation of this view. Unfortunately, there are some differences in the slopes of the straight lines obtained by plotting $\log a_{Zn}$ against $1/T$ (and hence in the values of $\bar{H}_{Zn}$ and $\bar{S}_{Zn}$ derived from both sets of data) which show that one of these methods was accompanied by systematic errors of unknown nature. However, the experimental data are consistent with themselves in each method of measurement, and a similar dependence of $\bar{H}_{Zn}$ and $\bar{S}_{Zn}$ values on the content of zinc may be derived qualitatively, see Fig. 8. It is probable that there are at least three regions in the α phase in which the partial heat of solution of zinc is practically constant but varies discontinuously at certain contents of zinc. The transitions between these regions occur at about 8.3 and 16.6 atomic pct Zn, i.e., at the ratios of

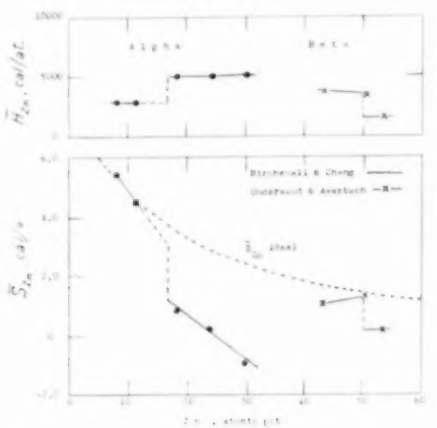


Fig. 9 (right)—Partial molar heat, $\bar{H}_{Zn}$, and partial molar entropy, $\bar{S}_{Zn}$, in AgZn alloys.

[Zn] to [Cu-Zn] equal to 1/12 and 1/6 respectively. These ratios may be probably connected with certain types of atomic arrangement in the face-centered lattice (coordination No. 12). On approaching a certain ratio from the side of lower zinc contents, a considerable short ordering of zinc atoms takes place which is reflected in the lowering of the partial entropy of zinc. An increase of zinc content above this ratio leads to the formation of a new type of atomic arrangement which is more disordered than the foregoing one. Still further increase of zinc content promotes a consolidation of the new configuration, and the entropy decreases again.

The measurements of zinc vapor pressures over AgZn alloys in the α phase made by Birchenall and Cheng[7] indicate the probable existence of at least two distinct regions for which the partial molar heat of zinc is practically constant, see Fig. 9. Alloys containing 7.3 and 10.5 atomic pct Zn are completely disordered, whereas the alloys between 17 and 29 atomic pct Zn must have an appreciable degree of order as can be judged from the lowering of the partial molar entropy of zinc. Precision measurements of lattice parameters in this system by Lipson, Petch and Stockdale[8] show interesting changes near 3, 17, and 29 atomic pct Zn. It was suggested by the authors that the parameter-composition curve of AgZn alloys consisted of four smooth curves intersecting at about these compositions. The data by Underwood and Averbach make probable the existence of two distinct regions in the β field of AgZn alloys.

The discontinuous changes as described above can be suspected in many other cases of homogeneous solid or liquid solutions. Since such changes may have their counterpart in changes of physical and technological properties of homogeneous phases, a detailed accurate determination of thermodynamic properties of alloys appears to be highly desirable.

L. Seigle *(Sylvania Electric Products Inc., Bayside, N. Y.)*—The writer had the opportunity to design, construct, and put into operation the Hargreaves' apparatus used in the work of Underwood, et al., and was impressed with the utility of the dew-point method for the determination of vapor pressures when conditions are appropriate for its use. Certain facts lead to the belief, however, that the possibility of error due to changes in the surface compositions of the solid alloys brought about by the measurement process itself needs careful inspection. It seems possible that the difference in vapor pressures observed between bulk and powdered alloys in the present work is due to a greater depletion of zinc at the surface of the bulk than at the surface of the powder particles. In carrying out a determination a definite amount of zinc is extracted from the test specimen within a short period of time (a simple calculation shows that there is not enough zinc in the vapor phase alone to form a deposit which can be easily seen) in order to form a visible deposit of pure liquid zinc at the colder end of the quartz tube. This quantity vaporizes from a much smaller surface area in the bulk than in the powdered alloys, and the tendency for surface depletion is correspondingly greater in the bulk material. Relatively greater decreases in the concentration of zinc at the surface of the bulk alloys could explain the difference in vapor pressures between bulk and powdered alloys observed in the present work.

On the other hand, the explanation advanced by the authors to account for the higher zinc vapor pressures over the powdered alloys does not seem reasonable. To make a dew-point measurement it is necessary to transfer enough zinc through the vapor phase to form a visible deposit at a point about 6 in. distant from the specimen, and to establish the equilibrium temperature by repeated evaporation and condensation of this deposit. It is hardly conceivable that such a process can be carried out without transferring the minute quantity of zinc between high and low points on the particle surface, separated by only a few ten-thousandths of an inch, necessary to equalize the vapor pressure of zinc over these irregularities. Indeed, the very same "quite large" diffusion rate of zinc in the solid which is invoked by the authors to maintain equality between surface and interior compositions would alone quickly equalize the chemical potential of zinc over the entire surface, and eliminate any difference in vapor pressure between high and low points. The maximum increase in vapor pressure which can be expected from the decreased particle size of the fine powders is probably close to that calculated on the basis of the average particle size, and therefore negligible in comparison with the sensitivity of the dew-point method.

Table IV Comparison of $\Delta\bar{H}$ Calculated by Different Methods

X_{Zn}	$\Delta\bar{H}_{Zn}$, Cal per Mol	
	Birchenall et al.[7]	Herbenar, et al.[9]
0.05		9300
0.0758	2420	
0.1053	2850	8100
0.15		7100
0.1733	4920	
0.20		6350
0.2345	5170	
0.25		5800

Certain peculiarities in the data of Birchenall and Cheng for α AgZn alloys also point to the necessity for caution in evaluating results obtained from the dew-point method, particularly when small differences are involved. The absolute value of $\Delta\bar{H}_{Zn}$ calculated from their data is compared in Table IV with the same quantity calculated from the data of Herbenar, Siebert, and Duffendack, who utilized a different experimental method.

The results of Birchenall and Cheng, which indicate an abnormal decrease in the absolute value of $\Delta\bar{H}_{Zn}$ with zinc concentration, are apparently incorrect. Although the evidence in this instance is very indirect, here again one is inclined to raise a question about the effect of concentration changes at the specimen surface as a likely source of error.

Niels Engel *(University of Alabama, University, Ala.)*—The Cu-Zn, Ag-Zn, and Au-Zn alloys exhibit very low free energy values of zinc at the noble metal end of the diagram and decreasing activities of the noble metals toward the middle of the diagrams. The explanation of this behavior is somewhat vague and is said to be caused by the energy difference between the hexagonal close-packed zinc and a hypothetical face-centered cubic zinc. An entirely different explanation of this behavior can be given.

In an earlier publication[4] I have postulated that the number of outer bonding electrons controls the lattice of metals analogous to the Hume-Rothery (8-N) rule phases. Thus one outer bonding electron controls a body-centered cubic lattice as found in the alkali metals, two outer bonding electrons control the hexagonal close-packed lattice as found for beryllium, magnesium, calcium, and a series of other metals, and three electrons control a face-centered cubic lattice. From this postulate the number of bonding d-electrons in the transition metals can be estimated.

The wave mechanical stipulations lead to the consideration of electrons in quantum states as rigid oscillators which cannot be changed unless the quantum state is altered. Based on this I have developed a new theory, termed the "electron oscillator theory" which accounts for the Cu-Zn, Ag-Zn, and Au-Zn phenomena under discussion and for many properties of metals and nonmetals. The theory is only partly published.[4] According to it, the interaction between two equal unpaired electrons should release about the same amount of energy by pairing under equilibrium conditions. If we assume the bonding energies of the different

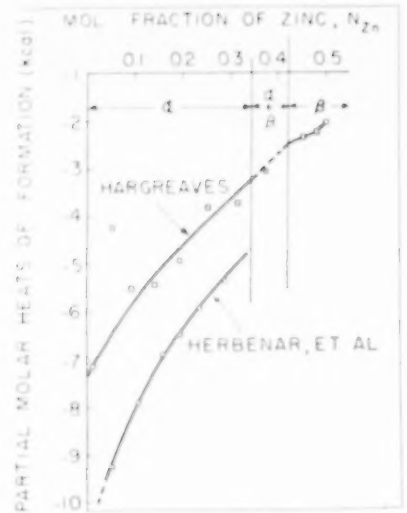
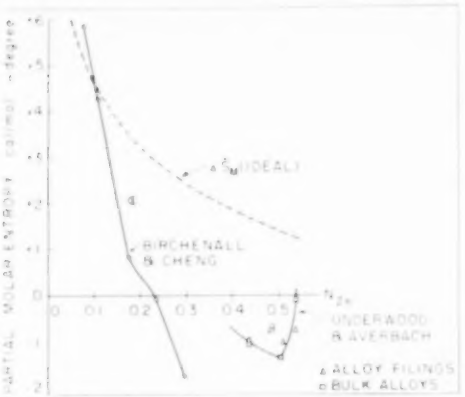


Fig. 10 (left)—Partial molar heats of formation of solid Cu-Zn alloys at 1100°K referred to solid zinc.

Fig. 11 (below)—Partial molar entropy of mixing solid Ag-Zn alloys at 620°C.



kinds of electrons to be as given in Table V, the ΔH values (ΔH value is the energy necessary to vaporize 1 g-atom of an element from solid at 273°C to a monatomic gas) of all elements can be calculated from the estimated electron distributions according to this rule. The numbers in Table V are taken from ref. 13.

According to this theory copper, silver, and gold must have the following electron-distributions:

Cu $1s^2\ 2s^2p^6\ 3s^2p^6d^{10}\ 4s^1$ shorthand writing Cu (4.5)[10]

Ag $1s^2\ 2s^2p^6\ 3s^2p^6d^{10}\ 4s^2p^6d^{10}\ 5s^1$ Ag (4.5)[10]

Au $1s^2\ 2s^2p^6\ 3s^2p^6d^{10}\ 4s^2p^6d^{10}f^{14}\ 5s^2p^6d^{10}\ 6s^1$ Au (4.5)[10]

If it is assumed that crystalline copper is formed of 75 pct Cu $(8)^1$ atoms and 25 pct Cu $(10)^1$ atoms, diamagnetism and other properties of copper can be accounted for.[10] Thus copper is considered as a transition metal which is in agreement with its high melting point, high Young's modulus, color and noble character. Cu-Zn, Ni-Zn, and Co-Zn form alloys of the same type containing Hume-Rothery α, γ, and ε phases,[14] whereas the Cu-Ni or Cu-Co diagrams are entirely different. Thus in alloys copper acts as a transition metal.

Alloying copper, silver or gold with zinc or other B group metals, the equilibrium $Ag\ (8)^1 \rightleftarrows Ag\ (10)^1$ shifts to the right partly because the average nuclear charge is increased and partly because the added atoms have closed d-shells. Diluting silver with atoms having complete inner shells must interrupt the d-electron bonds. By changing these bonds, silver atoms are transferred from the Ag $(8)^1$ state to the Ag $(10)^1$ state. By this change two d-electron bonds and two outer electron-bonds are broken. This work is equivalent to 2 (30 + 15) kcal per g-atom = 90 kcal per g-atom but only a part of the silver atoms can be transferred and the maximum amount is 75 pct.

In brass, because the α phase and the disordered β phase have random atom distribution, it must be assumed that several zinc atoms occupy lattice points with d-electron bonding and therefore are transferred to Zn $(8)^1$ or Zn $(9)^1$ atoms. Thus several zinc atoms are bonding with stronger d-electron bonding. This accounts for the low activity and vapor pressure in alloys with more than 40 pct Ag.

The commonly accepted viewpoint, that copper and silver are one electron metals and zinc is a two electron metal cannot account for the decreasing melting points, decreasing strength properties, decreasing vapor pressures, color and other properties of the copper column, B-group element alloys. The electron-oscillator theory accounts for these property changes by the interrupted d-electron bonds.

E. E. Underwood and **B. L. Averbach** (authors' reply)—It is difficult to justify discontinuities in the partial molar quantities $\Delta\bar{H}_{Zn}$ and $\Delta\bar{S}_{Zn}$ on the basis of the data presented by Dr. Herasymenko. These functions are very sensitive to slight experimental errors and the integral molar quantities would be more significant. Our data are presented in Figs. 10 and 11 and much greater accuracy is required before any discontinuous behavior in these functions can be confirmed.

A more detailed answer to the arguments of Dr. Seigle seems necessary, since they cast doubt on the validity of the dew-point method itself. His reasons for expecting no increase in zinc vapor pressure over the filings are convincing, but his explanation of the observed difference does not take into consideration all the facts available. He believes that the difference in vapor pressure between filings and bulk alloys is due to a greater depletion of zinc at the surface of the bulk alloys than at the surface of the powder particles. Why then should there be a difference of the same magnitude between the filed and the preheated powder particles of the same size as shown in Fig. 7? If the increased vapor pressure of the powders over the bulk is due, as he thinks, to lesser surface zinc depletion, then the preheated and as-filed powders should have essentially the same (increased) vapor pressures. But the preheated powders have the same vapor pressure as the bulk alloys (within 10 pct) and in fact, were usually less than the corresponding bulk alloy vapor

Table V. Bonding Energies of Different Kinds of Electrons

Period	Bonding Energy of $(s+p)$ Electrons Kcal per G-atom	Bonding Energy of d-electrons Kcal per G-atom
2	40	
3	20	
4	10	26
5	15	30
6	15	36

pressures (see Table I). Only the as-filed powders exhibited an increased vapor pressure.

Thus a consideration of the behavior of both types of powders obviates the line of reasoning adopted by Dr. Seigle. Our proposed explanation of the experimentally observed difference in vapor pressures may still be correct, although other explanations would certainly be welcome.

As for the doubts cast upon the sensitivity and the applicability of the dew-point method itself, one need only compare data from this method against that obtained in other ways. For example, activities of α CuZn alloys derived from the dew-point, absorption spectra, weighing and carrier gas methods[7, 8, 9] show the dew-point data to be as good as any. The same result is also shown by Weibke and Kubaschewski[10] in a comparison of ΔH_{298} for CuZn alloys, obtained from electromotive force calorimetric, and dew-point measurements. The authors are grateful to Dr. Seigle for his assistance in the construction of the apparatus.

[7] H. Lipson, N. J. Petch, and D. Stockdale: *Journal Inst. Metals* (1941) 67, p. 79.

[8] N. Engel: *Kemisk Maanedsblad* (1949) 30, p. 53.

[9] M. Hansen: *Aufbau der Zweistofflegierungen*. Berlin (1936) Springer.

[10] T. Schramm: *Ztsch. Metallkunde* (1938) 30, pp. 122, 327.

[10] F. Weibke and O. Kubaschewski: *Thermochemie der Legierungen*. (1943) p. 231. Springer-Verlag.

Effect of Temperature on the Lattice Parameters of Magnesium Alloys

by B. L. Busk

DISCUSSION, M. A. Williamson presiding

Niels Engel (*University of Alabama, University, Ala.*)—In this paper it was pointed out that the electron-gas and energy-band theory accounts for the fact that the lattice parameters exhibit a sudden change when the electron concentration (number of bonding electrons per atom) exceeds a certain number around two. This statement is said to support and prove the electron-gas theory. But this theory is not able to account for a series of experimental data. Also several expectations, deduced from this theory, are not found to exist. In Figs. 6 and 7 the energy bands of the second and third periods are given as they must be assumed in order to account for the electrical properties of the elements in these periods.

In Figs. 6 and 7 the electron-gas and energy-band theory is compared with the electron-oscillator hypothesis in accounting for the properties of the elements in the second and third periods. Fig. 6 shows the second period. The energy-bands are overlapping and separated to be in agreement with the electrical conductivity of the elements. The oscillator hypothesis explains conductivity due to electron vacancies. In graphite there is a closed *s*-shell in every other atom and two vacancies in the others. Conductivity is therefore only maintained by migration of *s*-electrons in graphite. In boron there are no *s*-electrons. The diatomic molecules of nitrogen and oxygen and the paramagnetism of oxygen can be accounted for by a similar behavior as the *s*-electrons of the bonding electrons. But this explanation will deviate too much for the purpose of this discussion. Fig. 7 shows the third period. In the energy-band picture about two *s*-electrons are assumed in magnesium and aluminum, but only one *s*-electron is assumed in silicon. The diamond lattice is assumed to be controlled by a sp^3 hybrid. However the electron distribution develops ideally according to the oscillator hypothesis. Only sodium, magnesium, and aluminum exhibit electron vacancies and conductivity.

To account for the insulator properties in Si, P, and S in the third period it must be assumed that the four last added *p*-electrons must be taken up in bands containing only one electron per band.[1] (Compare the electron band picture in Hume-Rothery.[1] Hume-Rothery does not consider the insulator properties of the nonmetals.) In the second period already the first *p*-electron must have entered a single electron band.

Based on the energy-band picture in Figs. 6 and 7, the following questions must be asked:

1—Is it consistent with the energy-band idea that electrons of the same kind (*p*-electrons) can be divided into separated bands?

2—Is it consistent with the energy band idea that single electron bands can exist?

3—Why are the first two *p*-electrons (in boron and diamond) separated into two single electron bands in the second period, but overlapping in the third period (aluminum)?

4—Why are *s*-electrons and *d*-electrons taken up in continuous overlapping bands, while *p*-electrons are divided into single electron bands?

5—Why do the peaks and valleys (y and w and further x and z) of the energy band below four electrons per atom not show up in the electrical conductivity of alloys? For example consider the Li-Mg system or the alloys between Mg and three electron metals where the mentioned discontinuity in the lattice parameter is found.

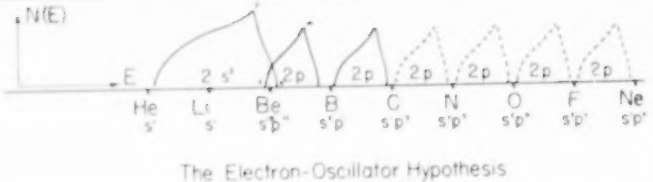
6—Why does the beginning of the *p*-electron band (x) not show up in the lattice constants similar to the filling up of the *s*-electron band (z)?

In magnesium alloys the electron-gas theory postulates the first Brillouin zone to be filled at about two electrons per atom. This is claimed to explain the sudden change in lattice spacing and c/a values of several magnesium alloys when the electron concentration exceeds a few percentage points over two electrons per atom. This was emphasized in the paper by Busk. If the electron-gas energy-band theory is correct a sudden change in electrical conductivity and possibly other properties should be expected when the same electron-concentration or temperature is exceeded. A sudden change in lattice spacing or other properties should also be expected when the filling degree is such that *p*-electrons are introduced into the *p*-band, for example at x in Figs. 6 and 7. Such phenomena are not found by experiment.

If the number of electrons should vary with the energy level depending on the average number of bonding electrons per atom, the electrical conductivity should be expected to vary in accordance with the energy band layout (Figs. 6 and 7) caused by different numbers of conducting electrons at different filling up degrees. Nothing indicating such a behavior is observed. In addition to these discrepancies between the electron-gas and energy-band theory and measured data, the theory violates the principles developed along with the Bohr theory of atomic structure. According to these principles a filled shell is saturated and therefore unable to form bonds. Therefore two *s*-electrons per atom should form a closed or saturated shell, which has been pointed out as accounting for the inability of helium to form bonds. Beryllium, magnesium, or calcium atoms with two *s*-electrons should be expected to form inert atoms with properties almost like the helium atoms.

Several other inconsistencies and disagreements with measured data of the energy-band theory can be mentioned. Some of these are discussed with reference to other papers.[2]

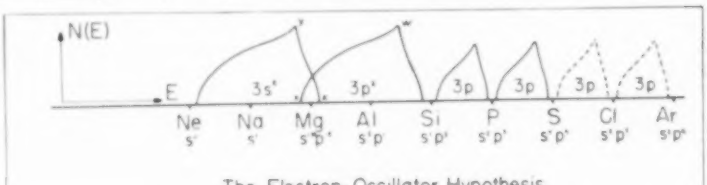
Because the electron-gas and energy-band theory seems to fail on several points, I have developed another theory which can account for all the phenomena the electron-gas theory is able to account for. This new theory is further able to account for things which are impossible to explain by the electron-gas theory at the present state.



The Electron-Oscillator Hypothesis

Total Number of Electrons		0	1	2	3	4	4	5	6	7	8
Paired Electrons within the Atom	s	0	0	0	0	1·2	0	2	2	2	2
	p	0	0	0	0	0	0	0	2	4	6
Bonding Electrons	s	0	9	99	0	0	1	0	0	0	0
	p	0	1	101	3	3	3	3	2	1	0
Vacancies		0	3	2	0	1·2	0	0	0	0	0
Electron-distribution		s²	s² p	s² p²	s² p³	s² p³	s² p⁴	s² p⁵	s² p⁶	s² p⁷	s² p⁸

Fig. 6 (left)—Second period of the electron gas and energy band picture, upper part, and the electron oscillator hypothesis.



The Electron-Oscillator Hypothesis

Total Number of Electrons		0	1	2	3	4	5	6	7	8
Paired Electrons within the Atom	s	0	0	0	0	0	2	2	2	2
	p	0	0	0	0	0	0	2	4	6
Bonding Electrons	s	0	9	98	1	1	0	0	0	0
	p	0	1	102	2	3	3	2	1	0
Vacancies		0	3	2	1	0	0	0	0	0
Electron-distribution		s²	s² p	s² p²	s² p³	s² p³	s² p⁴	s² p⁵	s² p⁶	s² p⁶

Fig. 7 (right)—Third period of the electron gas and energy band picture, upper part, and the electron oscillator hypothesis.

This new theory is called the electron-oscillator hypothesis and it can only be given very briefly in this discussion. I hope to be able to publish the theory in detail later. The electron oscillator hypothesis considers electrons in quantum states as rigid unchangeable oscillators. This statement is deduced from the wave mechanical stipulations. A single oscillating electron seeks to pair with another oscillating electron to cancel their fields. A particular oscillating electron can pair with another electron in the same atom forming a neutral pair. Such a neutral pair cannot bond atoms together. If no electrons are available for pairing within the same atom the unpaired electron can pair with an electron in another atom and form a bond between these two atoms. If non-paired electrons exist or can be created by the unpairing of one or more electron-pairs in a neutral atom, these non-paired electrons can form bonds with non-paired electrons in other atoms. Bonding of this kind is called homopolar bonding and, according to the electron-oscillator hypothesis, is due to cancellation of the fields of the non-paired electrons. This field cancellation is of essentially the same nature as pairing of electrons within the atom. It can be shown that interaction of non-paired electrons located in different atoms releases more energy than interaction or pairing within the atom. The first four electrons added to the outer ($s + p$) shell will normally remain capable of forming bonds with other atoms, see bottom of Figs. 6 and 7.

The electron distribution in the elements of the third period is given in Figs. 6 and 7. In sodium there will be an average of 0.9 s-electrons (maybe more) and 0.1 p-electrons (maybe less) per atom. Both s and p-electrons are paired with electrons from other neighboring atoms thus forming bonds. Because one s and three p quantum states can be occupied by electrons before pairing within the atom begins, there will be three vacant quantum states in the sodium lattice. In magnesium around 0.98 s-electrons and 1.02 p-electrons must be assumed. In the magnesium atoms no outer electrons will be paired within the atom and there will be two vacant quantum states. In the aluminum atoms we assume one s-electron, two p-electrons and no internal pairs and one vacancy. In the silicon atoms we find one s-electron, three p-electrons and no internal pairs and no vacancies. In the phosphorus atom two s-electrons pair within the atom leaving three bonding p-electrons and no vacancies, and so forth.

Electrical conductivity is accounted for on the following basis. Electrons occupying the same kind of quantum states require the same ionization energy and are therefore located at the same energy-level. At absolute zero temperature such electrons are at exactly the same energy level. With increasing temperature and increasing atomic vibrations the heat energy becomes superimposed on the ionization energy. Thus electrons of the same kind from different atoms will be located at different energy levels.

Only if vacancies are present among outer quantum states is electrical conductivity possible. Then electrons can jump from one quantum state to another in the same energy level. If no vacancies are present electrons must be elevated to the next higher quantum

state in the same or neighboring atoms before they can move and therefore insulator properties are created. According to Fig. 7, sodium, magnesium, and aluminum will be conductors and silicon, phosphorus, and sulphur will be insulators.

According to this theory a discontinuity at the point where all added electrons become p-electrons must be expected in the lattice parameter of hexagonal crystals and none in the electrical conductivity. This is because *s*-electrons have a ball shaped "electron-distribution" or field distribution and *p*-electrons have a directed "electron distribution" or bonding field. Therefore, *s*-electrons seek to maintain the same distance to all nearest neighbors whereas p-electrons only interact with one neighboring atom. This theory matches with almost all the data I know about.

The *s*-electrons have a ball shaped range of greatest interaction with other electrons and therefore form a body-centered cubic lattice, while p-electrons overlap in cigar-shaped regions. Two electrons force atoms into a close-packed hexagonal lattice and three electrons into a face-centered cubic lattice. This postulate accounts for many features interesting to metallurgists. A publication showing that this electron oscillator hypothesis can account for thermodynamic properties, magnetic properties, ferromagnetism and many diagrams and intermetallic phases has been published in Danish.[6]

[5] Hume-Rothery: *Atomic Theory for Students* (1948) p. 252, Fig. 114. London: Institute of Metals.

[6] See N. Engel's discussions on pp. 1214, 1221, 1226.

[6] N. Engel: Metals and Alloys as Electron Concentration Phases. Kgl. Danske Videnskabernes Selskab. Copenhagen (1949) 30, p. 53.

Correlation Between Electrical Conductivity and Temperature Coefficient Of Resistance of Solid-Solution Alloys

by M. Hansen, W. B. Johnson, and Jan M. Parks

DISCUSSION, M. A. Williamson presiding

J. K. Hulm *(University of Chicago, Chicago)*—The electron theory of metals throws some light on Hansen, Johnson, and Parks' empirical relationship between electrical conductivity and temperature coefficient of resistance. If the continuous solid solution data are included, this empirical relationship may be written in the general form:

$$\frac{1}{\rho_r} = \beta \frac{1}{\rho_r} \left(\frac{\partial \rho}{\partial T} \right)_r + \lambda \qquad [2]$$

where ρ is the electrical resistivity, the subscript r indicates room temperature values, and β and λ are constants of the following type:

1—For dilute solutions of different solute metals in a given solvent metal, β is constant and λ is zero.

2—For the continuous solid solution alloys of Group IB metals and their transition metal neighbors there are two cases: a—Systems like Pd-Pt in which single values of β and λ characterize the entire range of concentrations. b—Systems like Au-Pd in which the concentration range is split into two parts, each characterized by a separate pair of constants (β_1, λ_1) and (β_2, λ_2).

The electron theory of metals [7,8] indicates that the electrical resistivity of a solid solution alloy should be of the form:

$$\rho = D \cdot x(1\text{-}x) + B(x) \cdot T \qquad [3]$$

where the first term on the right hand side is due to scattering of electrons by the solute atoms, x being the fraction of solute atoms and D being a constant for a given pair of solute and solvent atoms. The second term is due to scattering of electrons by the thermally vibrating ionic lattice and the coefficient B is calculated to be:

$$B = \frac{3\pi^2}{2} \cdot \frac{m^2 a^2 C^2}{Mhke^2 \omega^2 N_v} \qquad [4]$$

where m and e are the electronic mass and charge, respectively; M is the atomic weight; C, the electron-lattice interaction constant; a, the lattice parameter; N_v, the number of conduction electrons per atom; and ω, the Debye temperature, the other symbols having their usual meaning. Since M, C, a, N_v, and ω will all depend upon the concentration x, B has been written as a function of x in eq 3.

It is now easy to interpret eq 2 under condition 1, since with λ zero, eqs 2 and 3 yield:

$$\beta \cdot B(x) = 1 \qquad [5]$$

For small values of x, B may be expected to be practically independent of the nature and concentration of the solute and to have a value characteristic of the pure, solvent metal.

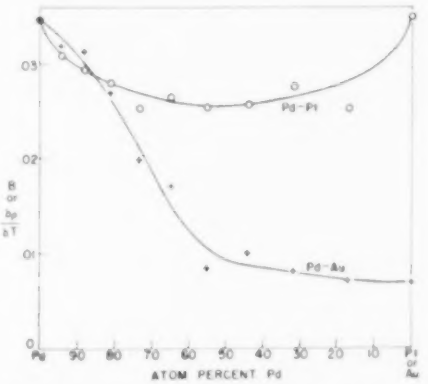


Fig. 15—Variation of B or $\frac{\partial \rho}{\partial T}$ with composition for the Pd-Pt and Pd-Au systems at 0°C, after Geibel.

Interpretation of eq 2, condition 2, is more difficult, but it is clear that nonzero values of λ are required to allow for the fact that B may change appreciably as x varies from zero up to 0.5 or more. Eqs 2 and 3 lead to the approximate relationship:

$$B(x) = [1 - \lambda \cdot D \cdot x(1\text{-}x)]/\beta \qquad [6]$$

and it is not really surprising that B can be represented, at least over a limited range, by a quadratic function of the type of eq 6. The fact that such a function is appropriate over the entire concentration range for the Pd-Pt system seems to originate in the coincidence that the B values for the separate pure metals are almost exactly equal,[9] as shown in Fig. 15.

It is interesting that the behavior of alloys of copper, silver, and gold with their transition metal neighbors, such as nickel and palladium, may be described by two pairs of constants (β_1, λ_1) and (β_2, λ_2), where the λ value applying to the copper, silver, or gold-rich half of the concentration range is effectively zero. Mott and Jones[9] have already discussed this phenomenon and postulate that in the copper, silver, or gold-rich half of the range the transition metal *d*-band is completely full, and the B value arising from the conductivity

contribution of the s-band electrons is practically independent of concentration, as shown in Fig. 15. In the transition metal-rich half of the range, the d-band is partially empty and there is an increased resistance due to s to d-band transitions, varying rapidly with concentration and thus requiring a finite s value. The nickel-rich region of the Cu-Ni system is not well represented by eq 2, a discontinuity in B being found at the composition where the ferromagnetic Curie point occurs at room temperature.

R. Smoluchowski *(Carnegie Institute of Technology, Pittsburgh)*—It is indeed interesting to see that there is that much apparent regularity in the behavior of electrical conductivity and of its temperature coefficient in various alloys. In general, from the elementary theory of conductivity, a rough proportionality would be expected between conductivity and the change of resistance. However, it is surprising that this parallelism extends to so many diverse systems. For binary alloys in which the two components have similar outside electronic structures, the relationship between the two quantities depends in the well-known manner upon the mass of the atom and the corresponding Debye temperature. It would hardly be expected that anything that simple would apply to alloys of transition metals whether they are ferromagnetic or not.

It is perhaps worth pointing out that the LeChatelier-Guertler rules as formulated by the authors are not generally applicable. Conductivity is not a linear function of volume percentage (Bi-Bi,Pb, Bi-Sn, Cd-Pb, Cu-Fe, Mg,Pb-Pb, Pb-Sb, etc.). Also it is not true that electronic resistivity is always lower in the pure metal than in a solid solution; an example here is the Fe-Co alloys in which after an initial rise the resistance drops below that of pure iron.

J. O. Linde *(Institutionen for Fysik I, Kungl. Tekniska Hogskolan, Stockholm, Sweden)*—For the description of the dependence of resistance on temperature in alloys, I introduce the resistivity-temperature coefficient $\alpha' = \frac{1}{\rho_o}\frac{d\rho}{dt}$. The numerical values of this coefficient can, in many cases, be approximated to those of the resistance coefficient $\alpha = \frac{1}{R_o}\frac{dR}{dt}$, or with fairly good approximation, the dilutation coefficient of the pure basic metal can be used in correcting α to α'. The empirical relation discussed in this paper may just as well be written:

$$\frac{1}{\rho_o} = k\frac{1}{\rho_o}\frac{d\rho}{dt} + c \qquad [7]$$

where ρ_o denotes the resistivity at 0°C and k and c are constants. As discussed by the authors, the constant c can, for different alloy systems, be positive or negative.

Eq 7 can be transformed into:

$$\frac{d\rho}{dt} = \frac{1}{k} - \frac{c}{k}\rho_o \qquad [8]$$

From eq 8 it can be seen that if $\frac{d\rho}{dt}$ (which quantity can easily be calculated from ρ_o and α') is plotted against ρ_o, the regularity concerned gives a straight line, the direction of which depends on c. Evidently $c = 0$ gives a line directed upwards, $c > 0$ downwards and $c = 0$ horizontally. Examples of curves corresponding to $c < 0$ are given in Fig. 16, taken from one of my publications.[5] In the figure ρ_r denotes the additional resistivity of the alloys. It can be seen from this, as well as from corresponding graphs for other alloy systems with b-metals (not transition metals) as added elements, that the deviation from Matthiessen's law (which law evidently is strictly obeyed in the case of $c = 0$) as a rule decreases with the valence, or group number, of the added element. According to my opinion, eq 8 is more appropriate for the analysis of experimental data of resistance of alloys (makes for instance possible a more sensitive representation of the results) than eq 7. A correction of α for the thermal expansion of the samples is not essential as long as only dilute alloys are dealt with, the relative value of the correction being rather small in these cases.

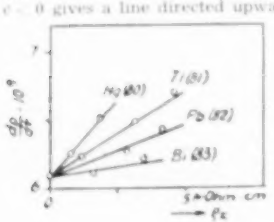


Fig. 16—Linear relationship between $\frac{d\rho}{dt}$ and ρ_o.

Niels Engel *(University of Alabama, University, Ala.)*—The electron-gas and energy-band theory is at present accepted as the theory which accounts for electrophysical properties. As pointed out in my discussion of Busk's paper,[6] the electron-gas and energy-band theory is not able to account for the insulator properties of silicon, phosphorus, and sulphur.

In the following it will be shown that this commonly accepted theory is unable to account for the temperature dependency of the electrical conductivity unless new reversing assumptions are added to the theory. In Fig. 17, a partly filled energy band at different temperatures is shown according to the energy-band theory. At absolute zero temperature the energy band is filled up to a very sharp upper energy limit. All quantum states with a lower energy content than this limit are occupied and no electrons occupy quantum states with higher energies. At intermediate temperatures the upper energy limit is somewhat diffused, which means that the quantum states in a certain energy region are partly filled and partly unoccupied. With increasing temperature this partly filled and partly vacant region increases. Each energy-level represents a quantum state or an electron moving through the lattice with a well-defined velocity and in a certain direction. Normally the vector sum of all directions and velocities of electrons at any point in a crystal must be zero. Applying an electrical field some electrons are elevated or depressed to other quantum states with movements directed toward the direction of the field. The vector sum becomes different from zero which is equivalent to a flow of electrons. From these assumptions, which are the assumptions of the electron-gas and energy-band theory, the number of conducting or free electrons (electrons which are able to change direction with a slight change of energy content) should be expected to increase with the temperature. The electrical conductivity should be expected to change in the same way. However experiment shows the opposite behavior.

To overcome this difficulty new assumptions are introduced by the electron-gas and energy-band theory and the old ones eliminated by philosophy. The new assumption is that the electrons in the electron-gas interact with the vibrating atoms. The more violent vibrations of atoms at higher temperatures increase the number of interactions between atoms and electrons and decrease the average free path length of electrons. A shorter free path length is concluded to decrease the flow of electrons. However if the average velocity of the electrons is constant (from Fig. 17 it can be seen that the average electron velocity of free electrons will be decreased slightly with increasing temperatures), and the probability of entering quantum states with vectors directed toward the direction of the field is unchanged, the average free path length of the electrons should not be expected to have any influence on the flow rate of electrons erected by a certain potential. Therefore this assumption is also unable to account for the temperature dependency of the electrical conductivity.

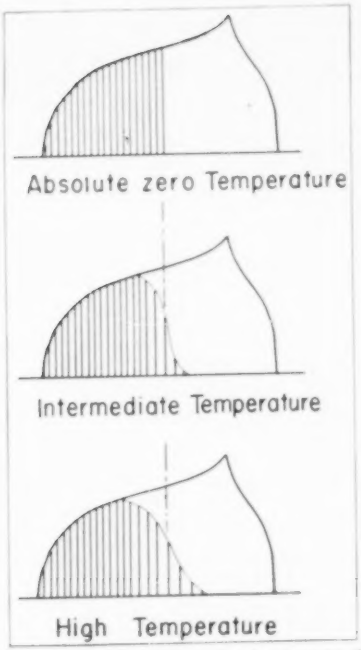


Fig. 17—Effect of temperature on the sharpness of the upper energy limit.

By working out the theory different authors introduce in their calculations either a temperature depending time the electrons are free or a dependency on the energy difference between vibrating atoms. The effect of the two first assumptions are either hidden or eliminated. The necessity of these assumptions therefore cannot be seen. A new theory not containing useless assumptions is therefore urgently needed. With the electron-oscillator hypothesis I hope to have made a useful suggestion.

The electron-oscillator hypothesis is founded on the wave mechanical stipulations. Electrons in quantum states are considered as oscillators restricted to vibrations with restricted amplitudes by the stipulation that the wavelength of the mass wave of the vibrating electron must be an integer on the path length of one period of vibration and thus controlling or quantizing the energy content of the electrons. Electronic oscillators are considered as unchangeable and each electron creates a field, which can be cancelled by pairing. Pairing of electrons can be established within the atom and such paired electrons are neutralized and cannot form bonds. Electrons not paired with another electron within the atom are able to pair with electrons in other atoms, thus forming bonds. Pairing resulting in bond formation is preferred. The way in which electrons pair and form bonds in the second and third period is given in ref. 26 in comparison with the energy-band picture.

In sodium there may be 0.9 *s*-electrons and 0.1 *p*-electrons all of which form bonds, but we do not know the exact distribution between *s* and *p*-electrons. The numbers are only a guess. When a particular electron forms a pair with an electron located in another atom, no further electron pairing with the first considered electron can occur in the atom. When four electrons from the same atom form bond pairs with electrons in neighboring atoms, no further electrons can be taken up in the atom by these four electrons without breaking bonds.

In sodium we have one bonding electron and three vacancies. In magnesium we have two bonding electrons distributed with about 0.99 *s*-electrons and 1.02 p-electrons and two vacancies. In aluminum there are 1 *s*-electron and 2 p-electrons and 1 vacancy per atom, and in silicon there are four bonding electrons and no vacancies. If vacancies are present, electrons from other atoms can move to these and occupy them and thus move or diffuse through the lattice. Atomic diffusion is supposed only to be possible when atomic vacancies are present.[27] Electronic and atomic diffusion are analogous. Therefore elements possessing electronic vacancies are metals and are electrical conductors. Nonmetals have no vacancies and are insulators. According to the electron-oscillator theory all electrons occupying the same kinds of quantum states have exactly the same energy. Electrons can jump from atom to atom without energy interchange with the surrounding world at absolute zero temperature in ideal lattices containing vacancies. Therefore such lattices are superconductors. By increasing the temperature atoms vibrate and bonds between atoms are partly broken. Then electrons will be situated at different energy levels. At higher temperatures electrons can only move through the lattice if the field from the applied potential is able to elevate the electrons from a lower to a higher level. The difference in energy levels between different atoms increases with temperature and the resistance also increases with temperature. This dependency can be exactly calculated on this basis for high as well as for low temperatures. From this theory the temperature dependency of the electrical conductivity should be expected to be the same for all metals as found by Hansen and coworkers. Only if the temperature changes alter the electron distribution, that is, some electrons are changed from, say, 4 *s* to 3 *d*- positions, should a deviation from this rule be expected.

The electron oscillator hypothesis is a rather new theory which has not been checked on all kinds of applications yet, but when applied on new unknown objects it seems to be able to account for several facts as shown in my contributions to other discussions.[28]

M. Hansen, W. R. Johnson, and **J. M. Parks** (authors' reply)—The volume of discussion is taken as indicative of a real interest in the subject. Dr. Hulm's discussion is a valuable addition to the appreciation of the fundamental origin of conductivity phenomena. We are pleased to note that the empirical analysis is not contradictory to fundamental tenets.

With regard to Dr. Linde's remarks, it is not felt that a plot of $\frac{d\rho}{dT}$ vs. ρ has any advantage over a plot of $\frac{1}{\rho}\frac{d\rho}{dT}$ vs. $\frac{1}{\rho}$ in the estimation of the magnitude of the constants, if due regard is taken of the significant figures for the data on ρ and $\frac{d\rho}{dT}$. In any least-squares solution for c, *k* (Linde) or *a*, *b* (Hulm), the same accuracy should be obtainable, although Dr. Linde's eq 8 is certainly less laborious to handle. Possibly Dr. Linde's scientific sensibilities are disturbed by plots of the type of Figs. 6 to 9. We would hasten to note that such a presentation is not intended to have scientific import, but rather to provide admittedly approximate, but very useful, engineering generalization. A proper evaluation of the effects of individual alloy additions must necessarily handle data for specific alloy systems individually, Figs. 4 and 5.

The method of data presentation, according to Dr. Linde's eq 8, is similar to that used by Norbury and Kuwada. His point that the line for a given system may be horizontal or skewed up and down is illustrated in Fig. 14, if rotated 90°.

It is likely that the Le-Chatelier-Guertler rule pertaining to heterogeneous mixtures of two phases is only valid to a first approximation. Unfortunately,

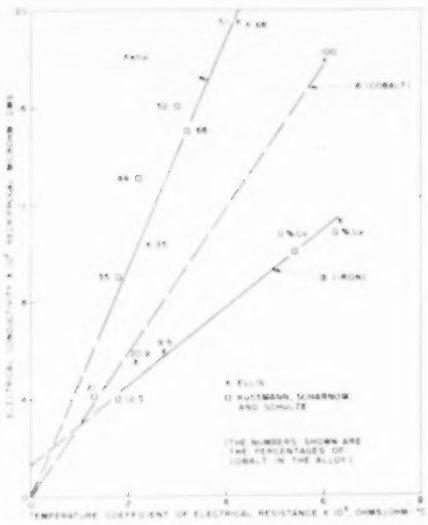

ELLIS
GUSSMANN, SCHARNOW AND SCHULTE
(THE NUMBERS SHOWN ARE THE PERCENTAGES OF COBALT IN THE ALLOY)
TEMPERATURE COEFFICIENT OF ELECTRICAL RESISTANCE X 10⁴, OHMS/OHM °C

Fig. 18—Electrical conductivity-temperature coefficient of resistance relationship in Fe-Co alloys.

there are, to our knowledge, no reliable data on the systems mentioned by Smoluchowski to substantiate his claims concerning rule 1. However, rule 2 is valid for all disordered solid solutions.

With regard to Dr. Smoluchowski's reference to the Fe-Co system and the higher conductivity of the ordered FeCo phase compared with respect to the ε-Co and the α-Fe solid solutions, an issue has been raised which was purposely omitted from the text of the paper because of lack of adequate, accurate data. From the data by Ellis, and by Kussmann, Scharnow, and Schulze, the electrical conductivity-temperature coefficient relationship is plotted in Fig. 18. Three lines are shown for each of the three phases: namely, the α-Fe solid solution, the ordered FeCo phase, and the ε-Co solid solution. Although there are insufficient points to substantiate the variations to be expected, there is good indication that the linear relationship is real. The same relationship is found when the data on the Cu-Au system is considered. A distinct conductivity-temperature coefficient line exists for each phase—Au_3Cu, AuCu, $AuCu_3$, and Cu—when the electrical conductivity is plotted vs. the temperature coefficient.

We look forward to amplification of Professor Engel's conductivity theory in some future publication. The statement is made in his discussion: "From this theory, the temperature dependency of the electrical conductivity should be expected to be the same for all metals as found by Hansen and coworkers." This appears to be a misunderstanding of the text, as no such statement was made or implied.

The authors have received a communication from Dr. W. Koster, Director of the Max Planck Institute for Metals Research, Stuttgart, Germany, which is believed to be of interest: "Your data and presentation have proved once more in a very clear way how nicely the old rule by Mathiessen is correct. This rule says that the product of the resistance of an alloy and its temperature coefficient is equal to the product of those two values of the pure metal, and consequently is a constant. If the resistance is replaced by the electrical conductivity, a straight line results which is, as shown in your paper, actually fulfilled. The β values given in Table I of the paper are Mathiessen's constants; that is, conductivity divided by the temperature coefficient of the pure metal."

[9] F. Seitz: *Modern Theory of Solids* (1940) New York, McGraw-Hill Book Co.

[10] N. F. Mott and H. Jones: *Theory of the Properties of Metals and Alloys* (1936) Oxford, Clarendon Press.

[11] W. Geibel: *Ztschr. anorg. allgem. Chemie* (1911) 69, p. 38 and 70, p. 240.

[12] J. O. Linde: Thesis, Stockholm (1939).

[13] See p. 1227.

[14] See pp. 1214, 1227.

Internal Friction Measurements on Iron Wires of Commercial Purity

by Arne Magnéli and Eric Ryde

DISCUSSION, M. A. Williamson presiding

L. J. Dijkstra and **R. Sladek,** *(Ontario Research Foundation, Toronto, and Institute for the Study of Metals, Chicago, respectively)*—This interesting paper confirms some results obtained some years ago in collaboration with Fast,[1] namely the broadening of the nitrogen peak by the presence of small amounts of manganese. Later on a more extensive study of this effect was made at the Institute for the Study of Metals at Chicago. As the work has not yet been submitted for publication we wish to mention here briefly some of the results.

The effect of about 0.5 atomic pct manganese, chromium, molybdenum, or vanadium on the nitrogen-peak in iron was examined. The broadening found previously in the case of manganese was even found to be more pronounced for chromium. In the case of molybdenum and vanadium a double peak was observed which seemed to justify the idea that in all cases mainly two relaxation times were involved: namely, the normal relaxation time as found in pure iron and a second relaxation time related to the existence of abnormal interstitial lattice sites introduced by the foreign metallic element. The analysis showed that for the normal nitrogen-peak as a reference at 22°C the abnormal peak was found at about 32°, 47°, 75°, and 87°C in the case of manganese, chromium, molybdenum, and vanadium, respectively. In the manganese alloy the free energy difference for a nitrogen-atom at an abnormal and a normal lattice site was estimated at 2800 cal per mol. This means that for temperatures above 100°C the solid solubility and overall diffusion rate of nitrogen is not much affected by additions of 0.5 pct Mn. We believe that the difference in rate of precipitation of nitrogen in pure iron and the manganese alloy is mainly a question of the number of potential nuclei available in the different steels.

In studying the effect of these alloying elements on precipitation of nitrogen, a distinction must be made between the para reaction and ortho reaction, using terminology introduced by Hultgren. The ortho reaction in which the alloying metallic element participates in the diffusion under formation of nitrides occurs at high temperatures such as 600°C. The para reaction in which the alloying metallic element does not diffuse and in which the nitride inherits its alloy content from the matrix occurs at lower temperatures. To prevent the ortho reaction the alloys have to be quenched rapidly from the γ phase. It is not surprising that the authors find that the height of the peak indicates a lower nitrogen content than chemical analysis. In the first place the peak is not a single relaxation peak and secondly, the steels were not quenched from the γ phase after the nitrogen was introduced at 580°C.

[1] A. Hultgren: *Trans.* A.S.M. (1947) 39, p. 915.

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aime NEWS

Electric Furnace Steel Men To Hold Tenth Anniversary Conference in Pittsburgh

THE Electric Furnace Steel Committee of the AIME will hold its Tenth Annual Conference at the Hotel William Penn, Pittsburgh, from December 4 to 6.

Operating men, repair and maintenance men, metallurgists, refractory and ceramic engineers, observers, and others who are interested in more steel, better steel, and cheaper steel will be on hand.

Conferees will have to make hotel reservations directly with the headquarters hotel or other Pittsburgh hotels. Included in the $7.00 registration fee is a bound copy of the Proceedings when they are published. AIME members are entitled to a $2.00 reduction in the registration fee on presentation of membership cards. No registration fee is required for students attending any of the sessions.

Highlighting the first day's activities will be a reception and cocktail party, followed by the Annual Fellowship dinner.

Preliminary Program of Electric Furnace Steel Conference

THURSDAY, DECEMBER 4

9:30 am

Joint Ingot and Castings General Session:

Chairman's welcoming remarks. Announcements and reports. Human relations in the furnace shop; statistical study of factors affecting production and quality; resume on use of oxygen.

2:00 pm

Joint Ingot and Castings Session on Fume Control:

Elimination of fumes and dust from electric furnaces; a unique approach to the collection of fumes.

6:30 pm

Reception and Cocktail Party

7:00 pm

Annual Fellowship Dinner

FRIDAY, DECEMBER 5

9:30 am

Ingot Session on Pit Practice and Refractories:

Gas heated hot tops; Autopour; the effects of melting practice on refractory consumption, furnace and ladles; standardization of electric furnace roofs.

9:30 am

Castings Session on Trends in Melting Methods:

Relation of power input and controls to efficiency and quality steel production; comparison of acid and basic steel for castings.

2:00 pm

Ingot Session on Furnace Practices:

Progress on temperature measurements; substitute sources of chromium for low carbon chromium stainless steels; current losses in roof cooling glands; preheating and scrap preparation.

2:00 pm

Castings Session on Quality Control and Present Melting Methods:

The addition of rare earth elements to common grades of steel; use of quantometer for rapid analysis; review of metallurgical practices and their effects.

SATURDAY, DECEMBER 6

9:30 am

Education Session (No Registration Fee):

Procedure in making a heat of stainless steel. Question period, panel of experts. The educational session is planned to be especially helpful to melters, helpers, observers, young metallurgists, and students. It has proved to be a very valuable refresher course to the regular registrants at the Conference.

E. W. Engelmann to Receive Richards Award

At the Board meeting on September 7, it was announced that Edward William Engelmann had been nominated to receive the Robert H. Richards Award at the annual meeting in 1953. The Board approved the nomination and the accompanying citation which reads: "For his outstanding accomplishments in advancing the technique of the metallurgy and beneficiation of copper ores."

Junior Application Procedure Changed

T. B. Counselman, Chairman of the Membership Committee, requested the Board to reconsider its action on Feb. 17, 1952 requiring that the signature of the original member sponsor be reobtained on the application for Junior Membership plus one more member's signature. The Board discussed this matter and voted that hereafter, a Student Associate applying for Junior Membership shall obtain only one member's signature, such signature to be other than that on his application for Student Associate. However, if he does not transfer in the year of his graduation, he must obtain the usual three members' signatures.

Initiation Fee Aids Local Section

The benefit to Local Sections in obtaining new members is not only an increase in membership but also financial aid. It may not be generally known that a Local Section receives $2 of the initiation fee of each new Member or Associate Member who resides in the territory of its Section. This does not apply to change of status nor to reinstatements. Until recently, only 10 per cent of any installment paid on the initiation fee was sent to a section but now the full $2 is sent at once although the full initiation fee may be paid if the member so wishes, in four equal installments. This addition to a section's working capital should be an extra incentive toward obtaining new members. Checks are mailed to Local Sections at approximately quarterly intervals.

Seek Recommendations For Kelvin Medal Award

Secretary Robie has received a letter from the Secretary of the Institution of Civil Engineers in London, England, requesting from each of the leading engineering societies in all parts of the world the name of a person recommended for the award of the Kelvin Medal in 1953. This medal, which was awarded for the first time in 1920, is presented triennially as a mark of distinction in engineering work or investigation of the kinds with which Lord Kelvin was especially identified. Although Lord Kelvin was pre-eminently a pioneer in the study of pure physics, he also achieved a great deal in the application of pure science to the solution of engineering problems. It is stressed, therefore, that the Medal be awarded to men of distinguished service in the application of science to engineering rather than in the development of physical science itself. The AIME has been requested to send a recommendation for this award before Feb. 1, 1953. A short statement of the grounds upon which the recommendation is made should accompany the nominations. Secretary Robie will be glad to consider any recommendations from AIME members for presenting to the Board for final selection.

Dues Bylaws Revised

In view of the authority given by the Board by referendum of the membership, at its meeting in Chicago on September 7, the Board voted to revise the first two sentences of Article II, Sec. 2 of the Bylaws to read as follows:

"Until otherwise determined by the Board of Directors of the Institute, the dues of Members and Associate Members shall be $20 per annum, and dues of Junior Members shall be $12 per annum for the first six years of membership and thereafter $17. Dues shall not be required of Honorary or Senior Members."

1953 Rand Medal Recipient Named

William E. Wrather, Chairman of the Charles F. Rand Foundation Award Committee, notified the Board of Directors that Eugene Holman had been nominated by the committee to receive the Charles F. Rand Medal at the annual banquet in 1953.

Install New Addressograph

Modernization of operations at AIME headquarters called for new addressograph equipment. The change-over to the new stencils was completed in time to run the wrappers for the October issues of the Institute journals. In changing the tabbing on 20,000 stencils, it is possible that some mistakes were made. If the wrong journal was received or too many copies, notify Institute headquarters.

— Coming Events —

Oct. 30-31. AIME, Fuels Conference, Coal Div., AIME; Fuels Div., ASME, Bellevue-Stratford, Philadelphia.

Oct. 31. Metropolitan Brass Founders Assn., Inc., show and dance, Hotel New Yorker, New York.

Nov. 1. AIME, Morenci Sub-section, Longfellow Inn, Morenci, Ariz.

Nov. 5. AIME, Chicago Section, Chicago Bar Assn., Chicago.

Nov. 6. Society for Applied Spectroscopy, Society-Vacuum Training Center, New York.

Nov. 7. AIME, Pittsburgh Section, National Open Hearth Steel Committee, off-the-record meeting, Hotel William Penn, Pittsburgh.

Nov. 8. AIME, Ohio Valley Section, dinner meeting, Beechwold Restaurant, Columbus, Ohio.

Nov. 8. ASTE, Chicago Chapter, annual mid-western tool engineering conference, University of Ill., Urbana, Ill.

Nov. 12. AIME, Connecticut Section, Hartford, Conn.

Nov. 18. AIME, Buffalo Section, National Open Hearth Steel Committee, Hotel Statler, Buffalo.

Nov. 19. Institute of Metals, lecture theater, Royal Institution of Great Britain, London.

Nov. 20-21. American Society for Quality Control, Midwest Conference, Claypool Hotel, Indianapolis, Ind.

Dec. 3. AIME, Chicago Section, Chicago Bar Assn., Chicago.

Dec. 4-6. AIME, Electric Furnace Steel Conference, Hotel William Penn, Pittsburgh.

Dec. 7-10. American Institute of Chemical Engineers, annual meeting, Hotels Cleveland and Carter, Cleveland.

Dec. 8. AIME, Arizona Section, all day meeting, Tucson.

Jan. 7, 1953. AIME, Chicago Section, Chicago Bar Assn., Chicago.

Jan. 14. AIME, Connecticut Section, Hammond Metallurgical Laboratory, Yale University, New Haven, Conn.

Jan. 26-30. American Society of Heating and Ventilating Engineers, international heating and ventilation exposition, International Amphitheatre, Chicago.

Feb. 4. AIME, Chicago Section, Chicago Bar Assn., Chicago.

Feb. 16-19. AIME, annual meeting, Statler Hotel, Los Angeles.

Mar. 9-11. American Institute of Chemical Engineers, Buena Vista Hotel, Biloxi, Miss.

Mar. 11. AIME, Connecticut Section, Waterbury, Conn.

Mar. 16-20. National Assn. of Corrosion Engineers, annual conference and exhibition, Hotel Sherman, Chicago.

Mar. 23-27. ASM, western metal congress and exposition, Pan-Pacific Auditorium, Los Angeles.

Apr. 12-May 23. Empire Mining and Metallurgical Congress, Australia-New Zealand.

Apr. 29-72. AIME, National Open Hearth and Blast Furnace, Coke Oven and Raw Materials Conference, Hotel Statler, Buffalo.

May 14-16. AIME Pacific Northwest Metals and Mineral Conference, joint meeting, Metals Branch and Industrial Minerals Div., Ben Franklin Hotel, Seattle.

June 3-7. Chemical Institute of Canada, Windsor, Ont.

Personals

Joseph T. Hobbs, Jr., metallurgical supervisor, is now assistant chief works metallurgist, Aluminum Co. of America, Alcoa, Tenn.

Charles L. Labeka is associated with the Pittsburgh Steel Co., Monessen, Pa., as chief metallurgist.

James M. Hall, formerly associated with the U. S. Steel supply div., U. S. Steel Co., Chicago, has accepted a position with the Fullerton Steel & Wire Co., Chicago.

J. W. Ribotto has been named metallurgical engineer, Magna plant, Kennecott Copper Corp., Utah Copper div., Garfield, Utah. He had been mill foreman.

M. N. Sigovich, National Carbon Co., Pittsburgh, recently has been transferred to Kansas City, Mo.

Robert H. Ridgway is now associated with the Pittsburgh Metallurgical Co., Inc., Niagara Falls, N. Y.

Herbert W. Lloyd is now assistant metallurgist, American Brake Shoe Co., Mahwah, N. J.

James O. Light has been made open hearth superintendent for the National Tube div. of the U. S. Steel Co., Lorain, Ohio.

Strickland Kneass, Jr. is manager of the combustion control dept., Morgan Construction Co., Worcester, Mass.

Jean Guy Montpetit has accepted a position as supervisor with the Quebec Iron & Titanium Corp., Sorel, Canada.

Chester W. Spencer has joined the metallurgy laboratories staff of Sylvania Electric Products, Inc., Bayside, N. Y.

ROBERT STEINITZ

Robert Steinitz has been appointed research supervisor of the American Electro Metal Corp., Yonkers, N. Y.

William F. Chubb is now associated with D. P. Fisher Ltd., Wellington, New Zealand.

Paul L. Widener has accepted a position with the Kaiser Aluminum & Chemical Corp., Halethorpe, Md.

W. L. SMITH

Walter L. Smith has been elected vice-president in charge of operations and director of Chase Brass & Copper Co., Inc. He joined Chase in 1915. Prior to this appointment Mr. Smith had been works manager for the Chase Metal Works at Waterbury, Conn.

John S. Winston is now assistant professor of metallurgy at the Mackay School of Mines, University of Nevada, Reno. He had been associated with the U. S. Bureau of Mines, Rolla, Mo.

Arthur C. Willhelm, Jr. has become plant metallurgist for the International Silver Co., Wallingford, Conn. He had been nonferrous metallurgist at the Meriden, Conn. plant.

Russell U. Acton has been appointed to the staff of the Oak Ridge National Laboratory, Oak Ridge, Tenn. The atomic energy installation is operated by Carbide & Carbon Chemicals Co., a division of Union Carbide & Carbon Corp.

W. P. Wallace has accepted the position of lead engineer with the California Research & Development Co., Livermore, Calif. He previously had been on the staff at the University of California, Los Angeles.

B. D. Weaver is now superintendent of research and development, Tin Processing Corp., Texas City, Texas. Mr. Weaver formerly has been chief chemist for the Algoma Steel Corp., Ltd., Sault Ste. Marie, Ont.

Norman Dirks has joined Modern Steel Treating Co., Chicago, as technical director. He had been chief metallurgist for the Perfection Tool & Metal Heat Treating Co., Chicago.

Eugene V. Ivanso has been appointed director of metallurgical engineering and research at the Detroit Testing Laboratories.

M. M. Hallett, Sheepbridge Engineering Ltd., Chesterfield, England, has been made research and development manager.

C. Kerby Stoddard is now employed by the Titanium Metals Corp. of America, Henderson, Nev., as chief development engineer.

S. Frederick Magis has been named steel technologist at the Armour Research Foundation of Illinois Institute of Technology. Mr. Magis has been consulting engineer to various firms in the steel industry.

Robert J. Painter, treasurer and assistant secretary, American Society for Testing Materials has been elected executive secretary. **Raymond E. Hess,** formerly assistant executive secretary and editor, has been named associate executive secretary and editor in chief.

Obituaries

Appreciation of
Calm Morrison Hoke
by Florence E. Wall, FAIC

Calm Morrison Hoke, chemist and engineer, authority on precious metals, died at her home in Palisade, N. J., on July 13, 1952, of an embolism following a long illness with phlebitis.

Miss Hoke, a member of AIME since 1929, was born in Chicago, Aug. 25, 1887, the daughter of Samuel W. Hoke, a pioneer in the technology of platinum, and Utopia (Wright) Hoke. She was educated in the Chicago schools, started at Wittenberg College (Ohio), and received her A.B. in chemistry at Hunter College, New York in 1908. She returned to Chicago, took a B.S. there in biology, in 1910, and was continuing in graduate study when her father's purchase of a blow torch business plunged her into metallurgy.

It may be all very well for present-day employment counselors to say, "Solve your shortage of engineers by employing women." Calm Hoke used to say that when in her efforts to bring herself abreast of the new business, she tried to enter certain classes in engineering at Columbia, it was like blasting at a solid wall with her own blow torches. The principal objection to admitting her was that there never had been any women in those classes. As a compromise, she was admitted to the lectures in mining engineering, but not to the labora-

tory. However, she did receive her Master's degree in engineering—the first granted there to a woman—in 1913. Except for two seasons during World War I when she also taught chemistry at Columbia, Miss Hoke's entire professional career was devoted to business.

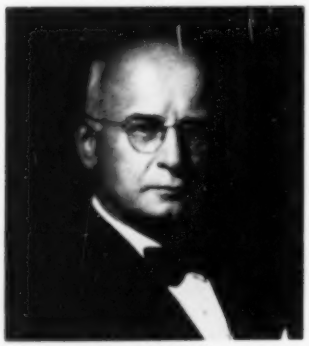
This was Hoke, Inc., and the associated Jewelers Technical Advice, established by her father in 1912. They soon held many patents for her inventions—small torches and burners, suitable for the delicate work of jewelers, which utilized ordinary illuminating gas instead of acetylene. She devised methods of extending the old touchstone method of testing gold and silver to the metals of the platinum group, then coming into use, and soon became an authority on the reclamation of precious metal wastes. She was vice-president and chief consultant of Hoke, Inc., from 1926 until the business was sold in 1934.

Through Jewelers Technical Advice, C. M. Hoke instructed jewelers, dentists, refiners, and many others in the melting, refining, salvaging, and finishing of all the precious metals. She gave many talks on the occupational opportunities in her unusual field, especially for girls in what she called gemology and metal book-keeping. She designed many beautiful pieces of jewelry, especially in platinum when it was very new. She had many calls for articles in the trade and professional journals; and her two books, *Testing Precious Metals* (1932) and *Refining Precious Metal Wastes* (1940) are classics in the industry.

Miss Hoke was a Fellow (and founder) of the American Institute of Chemists, and a Fellow of the AAAS; also a member of the American Chemical Society, the Electrochemical Society, the University of Chicago Alumni Women's University Club (N. Y.), and several other organizations that represented her wide diversity of interests. She will long be remembered by all that knew her in any capacity, professional or personal, because of her exceptional accomplishments, her engaging personality, and the generous understanding she gave to all their problems.

Although always known simply as C. M. Hoke, she was married in 1927 to T. Robert McDearman, and is survived by her husband, a civil engineer, now with the N. J. State Highway Dept.

Ralph H. Sweetser (Member 1894) died on June 29. Mr. Sweetser was born in Portsmouth, N. H. on Mar. 7, 1871. He attended Massachusetts Institute of Technology and graduated with the degree of B.S. in mining engineering and metallurgy. In 1892 he joined the Maryland Steel Co., Sparrows Point, Md., working at the blast furnaces. In 1897 he was superintendent of the Earlston furnace, Everett, Pa. He joined the Salem Iron Co. as assistant to the president. Mr. Sweetser joined the Cranberry Furnace Co., John City, Tenn. in 1902 as manager. He went to Canada a few



R. H. SWEETSER

years later and joined the Algoma Steel Co., Sault Ste. Marie, Ont. Returning to the United States in 1907, he accepted a position with the Columbus Iron & Steel Co., Columbus, Ohio. For three years he was president and general manager of the Thomas Iron Co., Easton, Pa. In 1917 Mr. Sweetser joined the American Rolling Mill Co., Columbus as works manager. He was appointed assistant to the first vice-president and was also vice-president of the Portsmouth By-Product Coke Co. In 1930 he was appointed assistant to vice-chairman, Armco. A Director and vice-president of AIME from 1925 to 1927, Mr. Sweetser was first Chairman of the Iron and Steel Div., and was Chairman of the Committee on Blast Furnace and Raw Materials. He was also a member of the American Iron and Steel Institute. In 1938 he wrote the book *Blast Furnace Practice*. He had been president of the Southern Ohio Pig Iron & Coke Assn. From 1930 until 1948 Mr. Sweetser was a consulting engineer practicing in New York.

NECROLOGY

Date Elected	Name	Date of Death
1943	William W. Avery	June 13, 1952
1926	Charles E. Bonn	July 17, 1952
1936	Henry M. Dalton	Sept. 29, 1952
1929	C. M. Hoke	July 13, 1952
1944	T. W. Pope	Sept. 6, 1952
1903	John J. Rutledge	Sept. 13, 1952
1893	Arthur L. Walker	Sept. 30, 1952

Proposed for Membership
— Metals Branch AIME —

Total AIME membership on Sept. 30, 1952 was 18,206; in addition 1383 Student Associates were enrolled.

ADMISSIONS COMMITTEE

T. D. Jones, Chairman; Thomas G. Moore, Vice-Chairman; Harold S. Bell, F. W. Hanson, R. H. Chadwick, T. W. Nelson, J. B. Knaf, John T. Sherman, A. C. Brinker, Ivan Given, C. A. R. Lambie, G. P. Lutton, E. A. Prentis, and C. Leslie Rice, Jr.

The Institute desires to extend its privileges to every person to whom it can be of service, but does not desire as members persons who are unqualified. Institute members are urged to review this list as soon as possible and immediately to inform the Secretary's office if names of people are found who are known to be unqualified for AIME membership.

In the following list C/S means change of status; R, reinstatement; M, Member; J, Junior Member; A, Associate Member; S, Student Associate.

Alabama
Birmingham—Boldon, Clarence C. (A)

California
Oakland—Harris, Frederick A. (M)
Richmond—Butler, Richard C. (J)—(C.S.—S-J)
San Mateo—Fitzwilson, Charles H. (M)

Colorado
Colorado Springs—Burgess, Thomas M. (A)
Denver—Lachmann, Walter J. (J)

D.C.
Washington—Canady, Donald W. (J)—(R.C.S.—S-J)

Florida
Bartow—Mayberry, Richard C. (J)

Illinois
Chicago—Carew, William F. (J)
Chicago—Philander, Herbert C. (M)
Oak Park—Dukette, George W. (M)

Indiana
Gary—Barker, George P., Jr. (J)

Massachusetts
New Bedford—Peterson, Eric G. (M)—(R.M)

Michigan
Detroit—McRoberts, Nelson L. (J)

Minnesota
Minneapolis—Gupta, Anika (M)

Missouri
Kansas City—Bailey, Frank E. (A)

Montana
Great Falls—Saylor, Clarence V. (M)

Nebraska
Omaha—Moran, Frank C., Jr. (J)

New Jersey
Perth Amboy—Jacob, Ernest M. (J)
Princeton—Meussner, Russell A. (A)
Ridgewood—Hamrick, Forrest G., Jr. (A)

New York
Belle Harbor—Feinland, Irving D. (M)
Bronxville—Sullivan, Robert C. (A)
Seneca Falls—Law, Jack M. (J)
Troy—Seymour, William E. (M)

Ohio
Columbus—Holladay, Joe W. (A)
Columbus—Klopp, William D. (J)
Columbus—Sabroff, Alvin M. (J)

Pennsylvania
Allentown—Seasholtz, Elwood F. (J)
Bethlehem—King, Parker P. (M)
Latrobe—Grobe, Arthur H. (M)—(R.C.S.—S-M)
Souderton—Fedusko, William (J)
State College—Zuckas, Victor F. (J)
Tamaqua—Turk, Roger R. (J)
West Hazleton—Hough, John W. (J)

Tennessee
Knoxville—Brasunas, Anton D. (M)—(R.C.S.—S-M)
Oak Ridge—Borie, Bernard S., Jr. (J)
Oak Ridge—Leighly, Hollis P., Jr. (J)—(R.C.S.—S-J)

Texas
Houston—Medlock, James D. (J)—(C.S.—S-J)
Kleberville—Manning, John A., Jr. (M)—(C.S.—J-M)

Washington
Cheverly—Stephens, Robert W. (M)
Pullman—Kleingard, Edwin N. (M)

Wisconsin
Janesville—Jensen, Jordan P. (J)—(C.S.—S-J)

Australia
Tasmania—Kirby, Noel S. (M)

Canada
Montreal—Dick, James G. (M)

Peru
Lima—Ralla, Jose H. (M)

Tokyo
Kyoheki—Winterhood, John S. (A)

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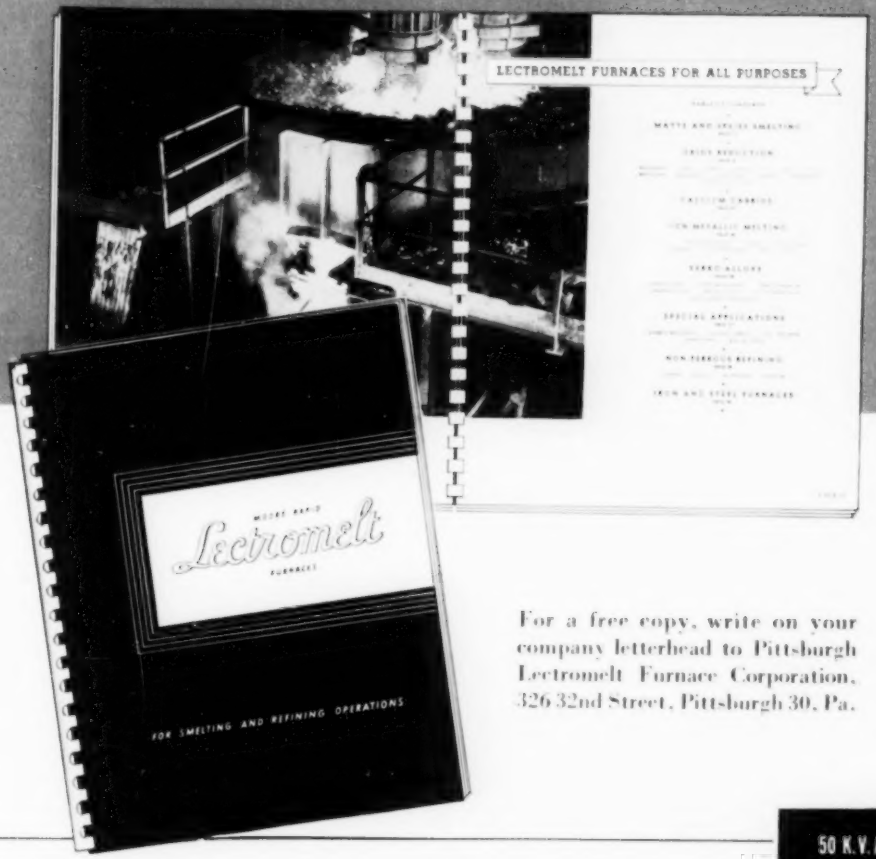

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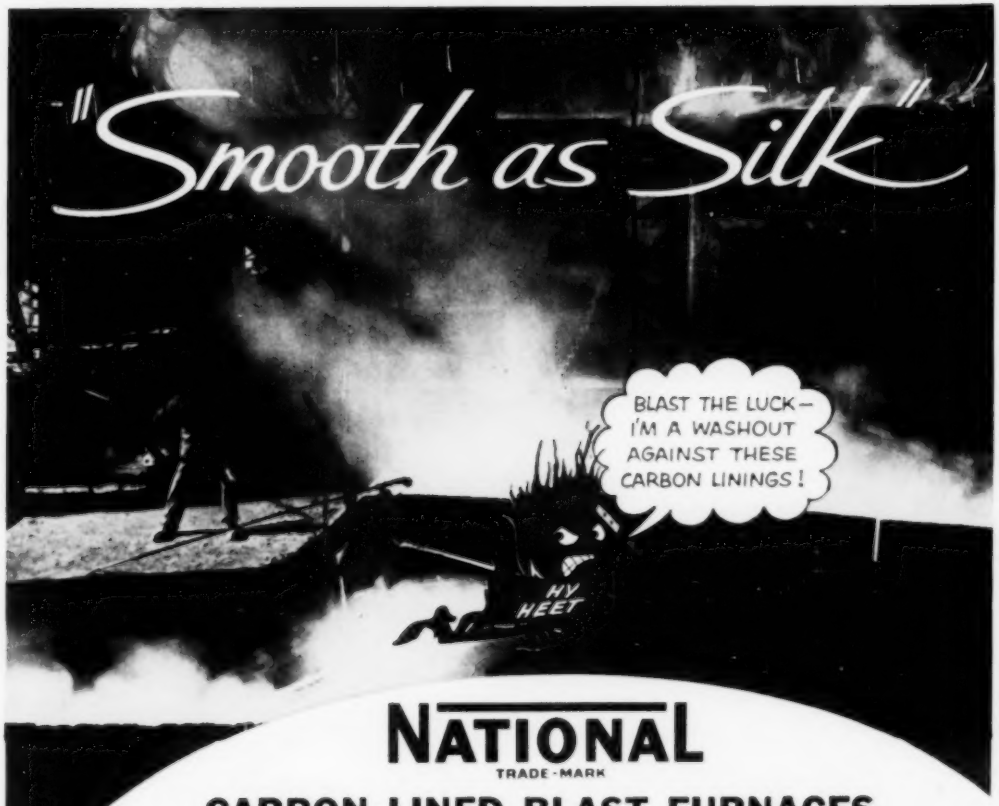

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